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KINETICS AND MECHANISM OF THE REDUCTION OF SULFOXIDES BY HYDRIODIC ACID

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KINETICS AND MECHANISM OF THE REDUCTION OF SULFOXIDES BY HYDRIODIC ACID

BY

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This thesis is dedicated to my parents whose guidance, understanding and encouragement aided me in the completion of this work.

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INTRODUCTION

This dissertation deals with the kinetics and mechanism of the reduction of sulfoxides to the corresponding sulfides by hydrogen iodide. The reduction of sulfoxides by a number of reducing agents has been known for quite some time.[1] However, the mechanism of these reductions has received relatively little attention.

Karaulova and Gallpern[2] used the reduction of sulfoxides with hydriodic acid as a method of preparing sulfides.

The first recorded study of the reduction of sulfoxides by hydriodic acid was by Allenmark.[3] From his experimental data Allenmark assumed that the first step in the reduction was a rapid attack of the electrophile H^+ upon the oxygen atom of the sulfoxide. This was followed by an attack of the nucleophile I^- upon the protonated species resulting in the formation of an intermediate M^+ which undergoes further reaction with I^- to give the observed products. The mechanism proposed by Allenmark is illustrated in Figure 1.

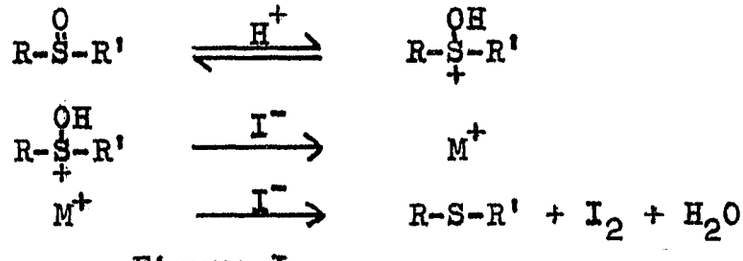


Figure I

The study carried out by Allenmark does not allow one to determine the point of attack by the nucleophile I^- upon the protonated species. The nucleophile can attack at the sulfur atom or at the protonated oxygen atom. Either of these points of attack will lead to the formation of the same products as illustrated in Figure 2.

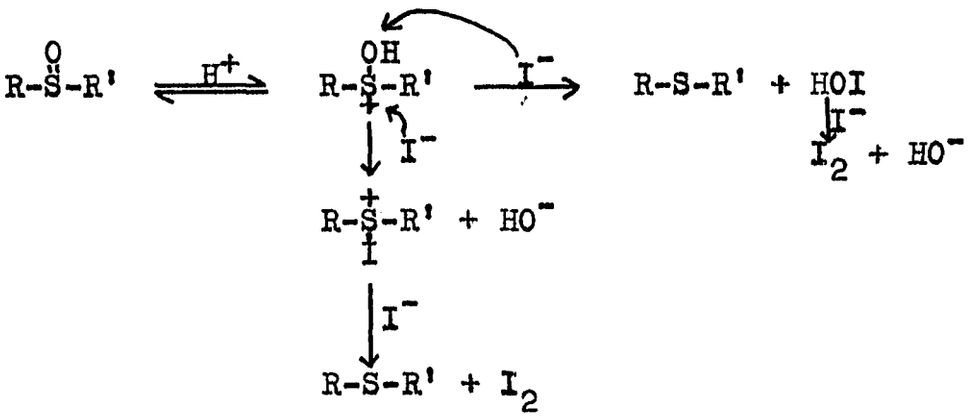


Figure 2.

The purpose of this work was to examine the mechanism of the reduction of sulfoxides by hydriodic acid and determine which of the reaction paths illustrated in Figure 2 was being followed or if there was another possible reaction path. At the time this work was started, the only publication concerning this study was that of Allenmark. Since then several investigators have published data pertinent to the mechanism of this reduction reaction.

Landini and co-workers[4] carried out studies similar to those presented in this dissertation. The same series of compounds were studied but in a different solvent system. The experimental results obtained by these investigators is in agreement with the experimental results presented in this

dissertation. However, the mechanism proposed by these workers does not completely explain the observed experimental evidence.

Krueger[5] has reported the reduction of dimethyl sulfoxide by iodide ion in acidic solutions of dimethyl sulfoxide-water solvent mixtures. A mechanism was proposed in which there was an iodide ion displacement of a leaving group from a positive sulfur center.

Since 1961, Allenmark has published several papers concerning the mechanistic aspects of the reduction of alkylsulfinylcarboxylic acids.[6,7,8,9]

RESULTS and DISCUSSION

I. Kinetic Order of the Reaction

A. Introduction

The reduction of sulfoxides by hydriodic acid is represented by the following equation:

$$R\text{-}\overset{O}{\overset{\|}{S}}\text{-}R' + 2H^+ + 2I^- \longrightarrow R\text{-}S\text{-}R' + H_2O + I_2 \qquad (1)$$

Allenmark[3] followed the reduction of some β-alkylsulfinylcarboxylic acids keeping hydrogen and iodide ions in excess. A plot of the log of the sulfoxide concentration versus time resulted in a straight line indicating that the reaction was first-order in sulfoxide and pseudo-first-order overall.

Landini and co-workers[4] studied the reaction using aryl alkyl and substituted phenyl methyl sulfoxides in aqueous acetic acid containing hydriodic acid. Their results indicated that the reaction follows a third-order rate law which was first-order with respect to sulfoxide and second-order with respect to hydriodic acid.

Krueger[5] has studied the reduction of dimethyl sulfoxide under conditions which maintained the sulfoxide in excess. His results indicated that the reaction was second-order in hydrogen ion and first-order in iodide ion. The reaction best fitted a rate law represented as:

$$\text{rate} = k\,(H^+)^2(I^-) \qquad (2)$$

B. Dependence of rate on sulfoxide concentration.

Several runs were carried out using phenyl methyl sulfoxide in which the hydrogen and iodide ions were kept in excess, and the concentration of the sulfoxide was varied as indicated in Table 1.

Table 1

The Effect of Sulfoxide Concentration on Reactivity

Sulfoxide, M	H^+, M	I^-, M	$10^5 k$, sec.$^{-1}$
0.010	4.0	0.20	22.23
0.005	4.0	0.20	22.34
0.001	4.0	0.20	22.45

The results obtained indicate that the reduction reaction is first-order in sulfoxide. This is in agreement with the results obtained by previous workers.

C. Dependence of rate on acidity.

Using phenyl methyl sulfoxide and maintaining hydrogen and iodide ions in excess, the reaction was run at several different acid concentrations as indicated in Table 2.

Table 2

The Effect of Acid Concentration on Reactivity

H^+, M	$10^5 k$, sec.$^{-1}$	log k + 5	$-H_0$
3.0	2.71	0.4330	1.23
3.5	7.42	0.8704	1.47
4.0	22.35	1.3493	1.72
4.5	59.01	1.7709	1.97

The H_o values were obtained from Paul and Long[10], and the results indicate that the reaction is acid catalyzed. Allenmark, Krueger, and Landini and co-workers also found this to be the case.

D. Dependence of rate on iodide ion concentration.

Phenyl methyl sulfoxide was reduced at a constant acid concentration of 4.0M while the iodide ion concentration was varied as indicated in Table 3.

Table 3

The Effect of Iodide Ion Concentration on Reactivity

I^-, M	10^5k, sec.$^{-1}$	10^4k, l/mole sec.
0.025	1.78	5.79
0.050	4.21	7.62
0.10	8.68	9.18
0.20	22.22	10.7
0.30	37.09	12.5

The results indicate that the reaction is dependent upon iodide ion and first-order in iodide ion. As shown by the change in rate constants with increasing iodide ion concentration, the rate follows most closely the second-order rate expression:

$$\text{rate} = k_{obs.}\ (\text{sulfoxide})\ (I^-) \qquad (3)$$

The slight increase in the second-order rate constants with increasing iodide ion concentration is due to an increase in the ionic strength of the reaction solution. Allenmark[3]

has found the reaction to have a positive salt effect. A plot of Allenmark's first-order rate constants[7] (zero-order in iodide and first-order in sulfoxide in 2.0M perchloric acid) versus the second-order rate constants listed in Table 3 (first-order in iodide and first-order in sulfoxide in 4.0M perchloric acid) gave a straight line as shown in Figure 3. The simplest explanation of the parallelism is that both reactions are influenced by the ionic strength in the same manner and that the reactions are of the order in iodide concentration as stated; zero-order for Allenmark's reaction and first-order for this reaction. A plot of Allenmark's first-order rate constants versus our first-order constants gave a curved line.

E. Dependence of rate on products

Several runs were carried out using phenyl methyl sulfoxide with the hydrogen ion concentration at 4.0M and iodide ion concentration at 0.20M. Sulfide and iodine were added to the kinetic solutions in order to determine the effect of the products formed on the rate of the reaction. Table 4 indicates that the products formed in the reaction have no effect on the rate of the reaction.

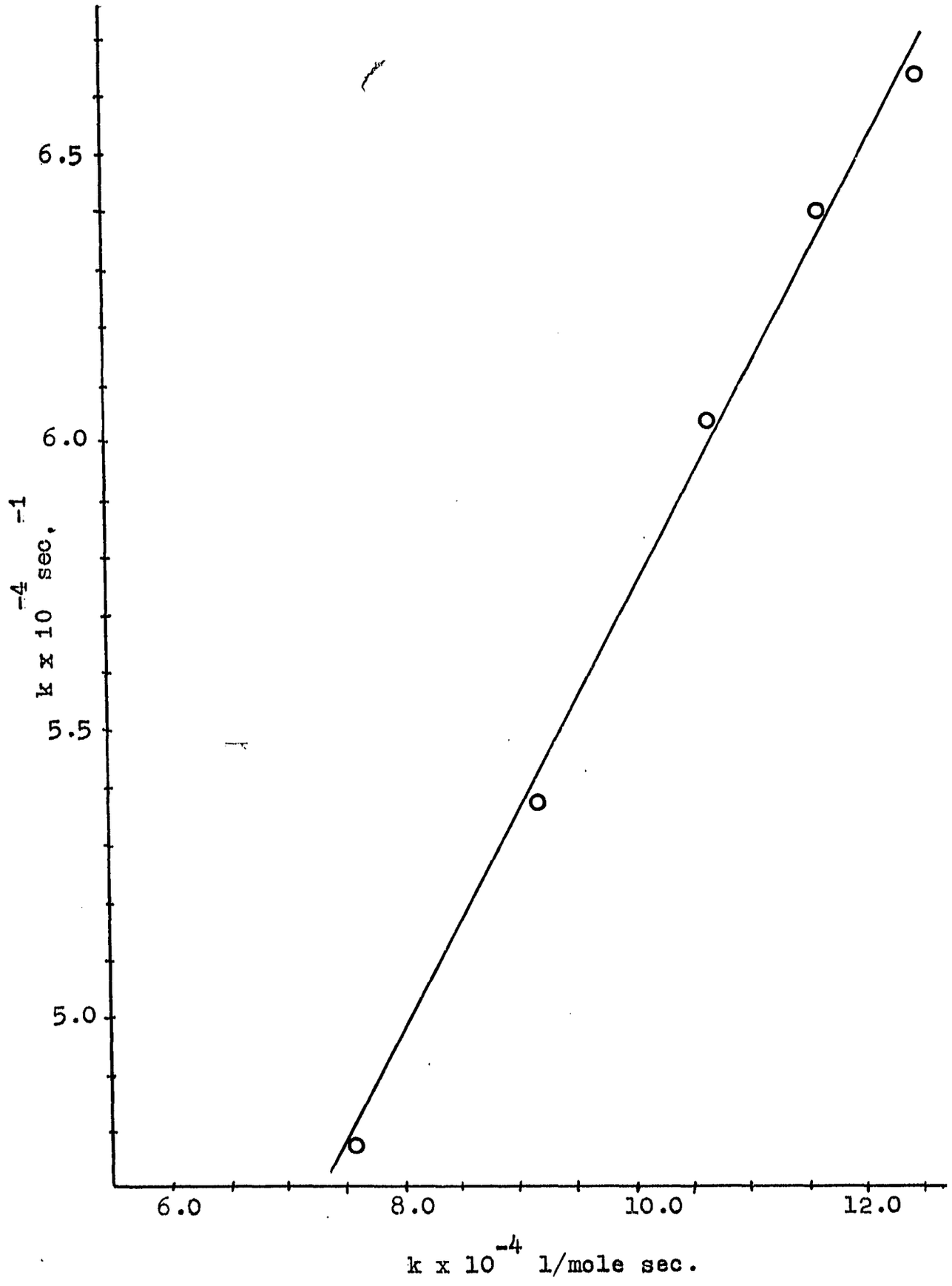
Table 4

The Effect of Products on Reactivity

$I_2 \times 10^{-5}$, M	Sulfide $\times 10^{-5}$, M	$10^5 k$, sec.$^{-1}$
2.5	-----	22.62
---	4.0	22.83
0	0	22.35

Figure 3

Plot of Allenmark's 1st order rate constants vs. 2nd order rate constants in Table 3.



II. Effects of Structure on Reactivity

A. Steric Effects

The reduction was carried out on several phenyl alkyl sulfoxides in which the alkyl groups were methyl, ethyl, isopropyl and t-butyl. Rate studies were also carried out on cis- and trans-4-(4-chlorophenyl)-thiane-1-oxide. The effect of increasing the steric bulk about the sulfoxide function is shown in Table 5.

Table 5

Steric Effects on Reactivity

C_6H_5SOX	$10^5 k, sec.^{-1}$
$-CH_3$	22.35
$-C_2H_5$	13.71
$-CH(CH_3)_2$	0.4560
$-C(CH_3)_3$	$\sim 10^{-2}$
Thiane-1-oxide	
cis-	4.43
trans-	103

The results indicate that as the steric bulk increases, the rate of the reaction decreases. Allenmark[6] and Landini[4] also observed a decrease in rate with increasing steric bulk. In the case of the cis- and trans-4-(4-chlorophenyl)-thiane-1-oxide, the trans isomer is reduced approximately 24 times faster than the cis isomer. This result is opposite to what

would be expected. A possible reason for the results obtained will be presented later in this thesis.

B. Inductive and Resonance Effects

The effect of meta- and para- substituents upon the rate of reduction of aryl methyl sulfoxides is given in Table 6.

Table 6

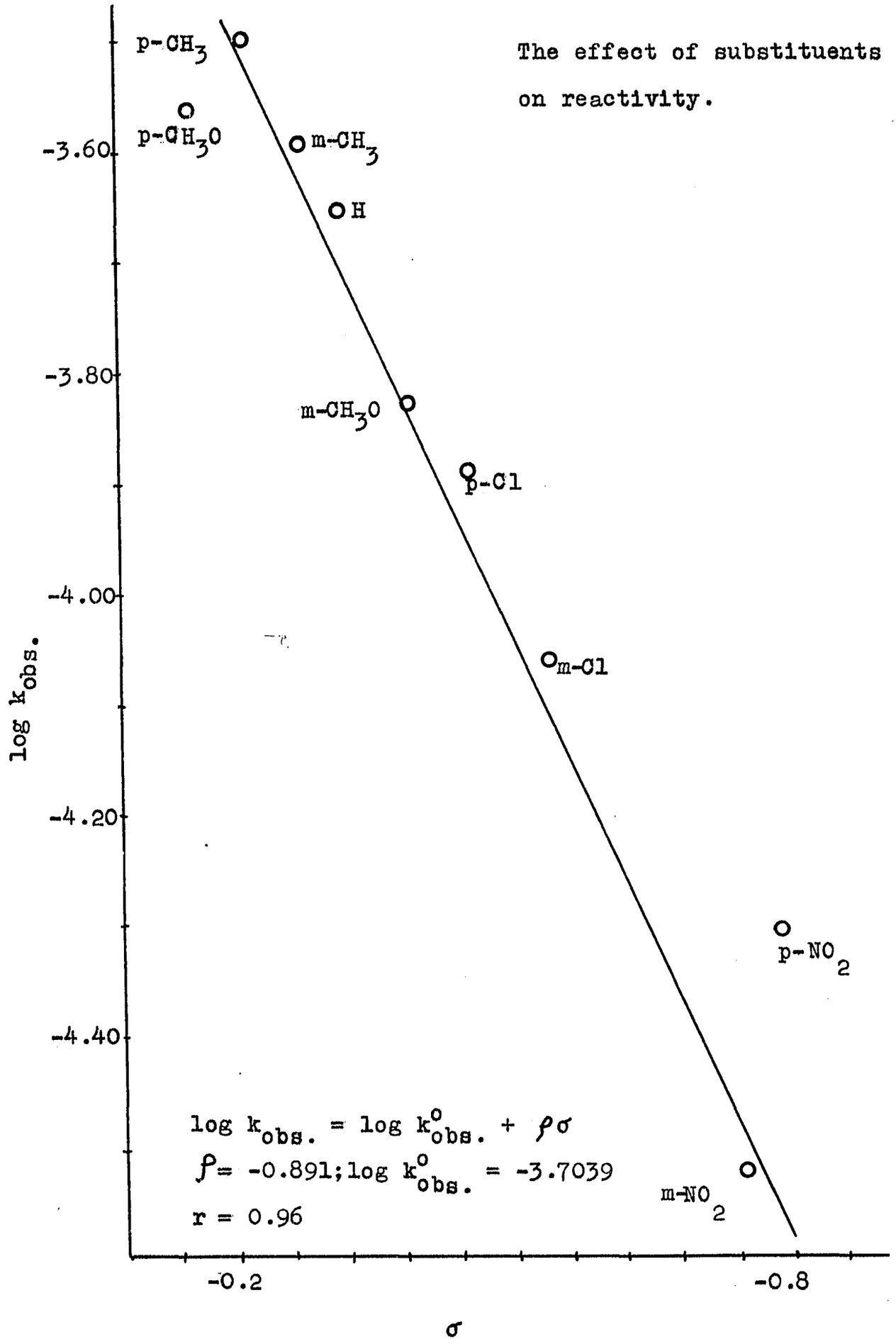
The Effect of Substituents on Reactivity

$X\text{-}C_6H_4SOCH_3$	$10^5 k_{obs.}$, $sec.^{-1}$	log $k_{obs.}$	σ^o
p-CH_3	31.69	-3.4991	-0.17
m-CH_3	25.60	-3.5918	-0.07
p-CH_3O	27.40	-3.5622	-0.27
m-CH_3O	14.91	-3.8265	+0.12
p-Cl	13.03	-3.8851	+0.23
m-Cl	8.73	-4.0590	+0.37
p-NO_2	4.98	-4.3028	+0.78
m-NO_2	3.37	-4.4724	+0.71
H	22.35	-3.6507	0.00

Application of the Hammett equation[11] results in a straight line when log $k_{obs.}$ is plotted against σ^o constants compiled by McDaniel and Brown[12] as illustrated in Figure 4. The line obtained has a ρ = -0.891 and a correlation coefficient of 0.962.

A plot of Landini's rate constants versus the rate constants in Table 6 for each substituent resulted in a fairly

Figure 4



The effect of substituents on reactivity.

good straight line as shown in Figure 5. This indicates that the different solvent systems used in the two studies do not cause a change in the effects of the substituents on the reaction.

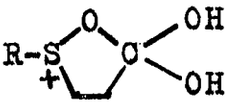
III. The Mechanism of the Reaction

Several mechanisms for the reduction of sulfoxides in the presence of hydrogen and iodide ions have been proposed. These mechanisms were determined under different conditions or on sulfoxides of different structure than those used in this study.

Allenmark's studies[6-9] on the reduction of β-alkylsulfinylcarboxylic acids in aqueous perchloric acid and sodium iodide yielded the following information. The reaction rate was independent of iodide ion concentration[7] and dependent upon the concentration of acid and sulfoxide.[3] The reaction had the following rate equation

$$\text{rate} = k\,(\text{sulfoxide})\,(H^+) \qquad (4)$$

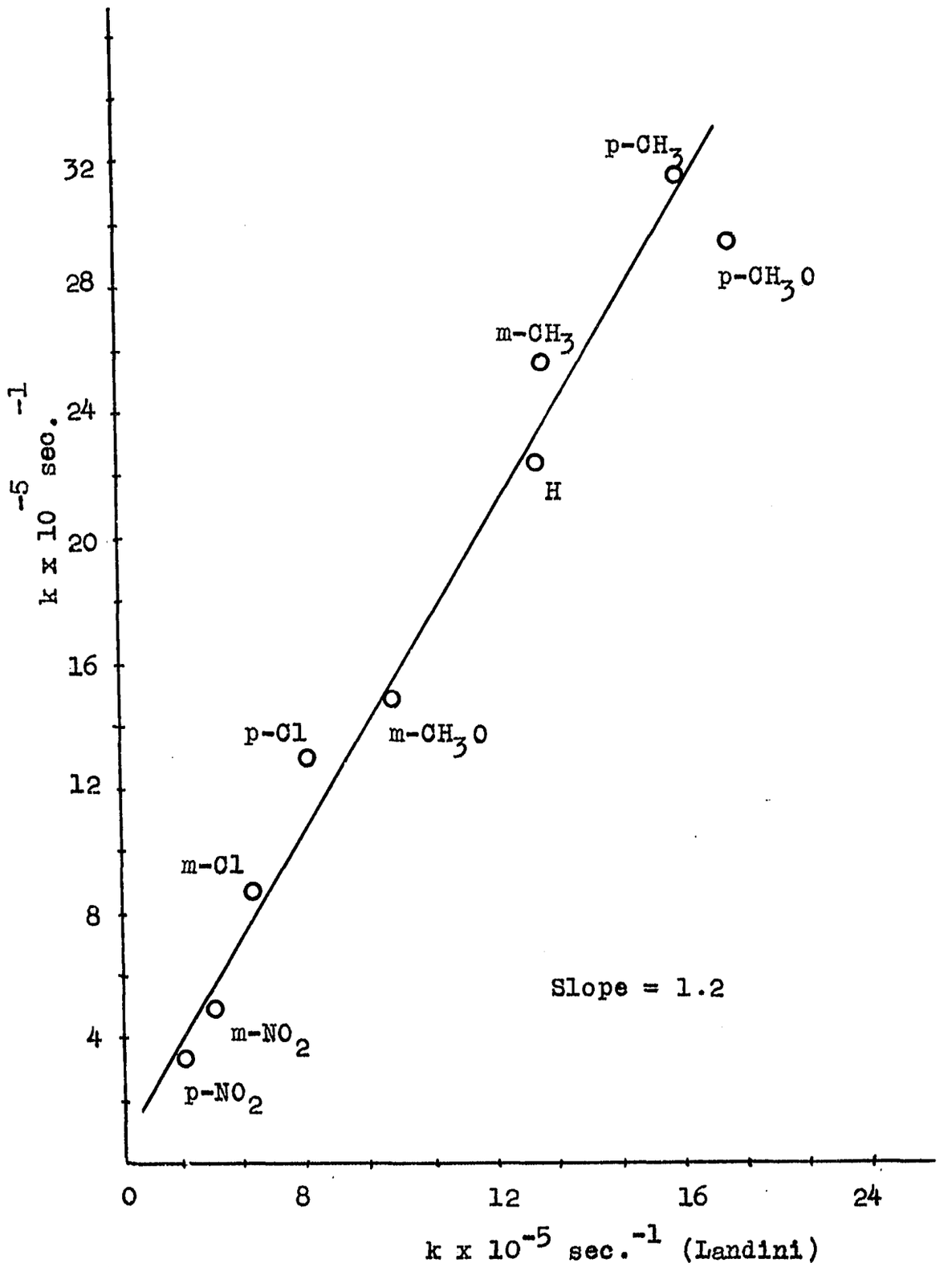
From studies of the activation enthalpy and entropy for the reaction[8] and studies on <u>cis</u>-<u>trans</u> isomeric α,β-unsaturated sulfoxide-acids, the hypothesis was made that a five-membered ring of the type:



existed as an intermediate in the reduction in acidic iodide

Figure 5

Plot of k values for meta- and para-substituted sulfoxides vs. Landini's values



solution, and that the formation of this intermediate is a rate-determining step. The studies on cis-trans isomeric α,β-unsaturated sulfoxide-acids gave the greatest support for the formation of a cyclic intermediate. A study of the reduction of β-benzylsulfinyl-trans-crotonic acid showed that it was reduced 100 times faster than β-benzylsulfinylpropionic acid under identical conditions, while no reaction at all was detected in the case of β-benzylsulfinyl-cis-crotonic acid. In the case of the cis isomer a cyclic intermediate of the type shown above is incapable of being formed.

Allenmark's plot of log k vs. $-H_o$ resulted in a straight line with a slope of unity.[3] Following Zucker and Hammett[13], the assumption had generally been made that correlation of rate by the acidity function requires a mechanism in which an acid-base equilibrium involving the substrate is followed by a unimolecular rate-determining step in which the conjugate acid of the substrate proceeds to products. This mechanism is illustrated by equations (5) and (6). Based upon this result, it was

$$S + H^+ \rightleftharpoons SH^+ \quad \text{(equilibrium)} \qquad (5)$$

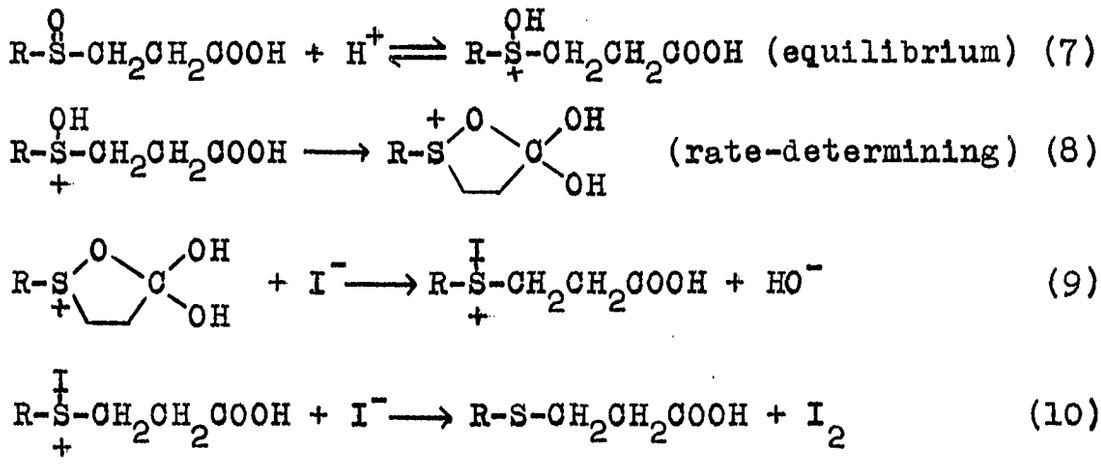
$$SH^+ \longrightarrow \text{products} + H^+ \quad \text{(rate-determining)} \qquad (6)$$

assumed that the first step in the reaction is a rapid proton-sulfoxide equilibrium. However, the Zucker-Hammett postulate has been shown to be invalid.[14]

Sulfoxides are weak bases[15,16]; the oxygen terminal of the sulfoxide function is capable of accepting protons.[17] This

is supported by studies on hydrogen bonding with sulfoxides where the infrared stretching frequency of the sulfoxide is decreased due to bonding through the oxygen. If bonding occurred through sulfur, the stretching frequency would be increased.[18] Allenmark[6] recorded the infrared stretching frequencies of some β-alkylsulfinylcarboxylic acids in water and in 2M hydrochloric acid. It was noticed that the $\rangle S{=}O$ absorption generally occurred at a lower frequency for these compounds than for dimethyl sulfoxide (neat).

Using the preceding information, one can postulate the following mechanism for the reduction of β-alkylsulfinylcarboxylic acids.



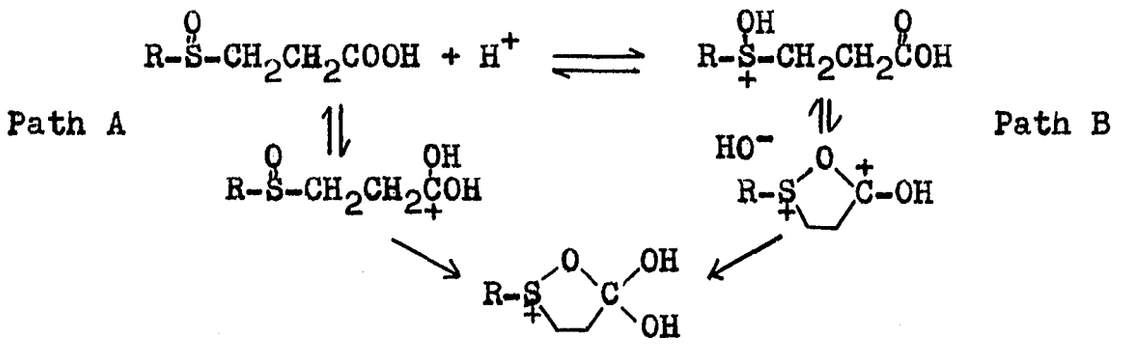
This mechanism is in agreement with the general mechanism proposed by Zucker and Hammett for a reaction that gives a correlation of rate by the acidity function. There is no kinetic evidence bearing on the validity of (9) and (10) which have been introduced to indicate a reasonable path leading to final products.

Allenmark does not indicate how the cyclic intermediate

is formed in the rate-determining step of the reaction. Figure 6 illustrates two possible paths to the cyclic intermediate.

Figure 6

Possible paths to Allenmark's cyclic intermediate



Path B would appear to be favored over Path A. The size of the R- group attached to the sulfur has an inhibitory effect on the rate as R- is increased in size as indicated in Table 7. The size of the R- group should have very little

Table 7

Steric Effect on the Reduction of β-Alkylsulfinylcarboxylic Acids

R-	10^3k, $min.^{-1}$	C_{H^+}
$CH_3CH_2CH_2-$	10.6	1.00
$(CH_3)_2CH-$	3.5	1.50
$(CH_3)_3C-$	$\sim 10^{-2}$	2.00

effect on the rate of the formatiom of the cyclic intermediate if Path A is followed. Also, the greater basicity of the sulfoxide oxygen compared to the carbonyl oxygen would favor protonation of the sulfoxide oxygen first.

Substituting two methyl groups for the two β-hydrogens on the sulfinyl carboxylic acid where R- is n-propyl increases the reaction rate from 10.6 x 10^{-3} $min.^{-1}$ to 25.8 x 10^{-3} $min.^{-1}$. This rate enhancement could possibly be due to inductive stabilization of the positive sulfur by the added methyl groups on the adjacent carbon.

Any attempt to explain the observed rate increase based on the possibility that the addition of the methyl groups results in a conformation which places the carboxyl group in a more favorable position for attack on the positive sulfur would be unreasonable at the present time. The role of lone electron pairs on sulfur in conformational analysis is not really understood, and Mislow[19] has pointed out that "conformational rules emperically derived from one type of system may not be legitimately extrapolated and transferred to another".

Based upon the information available at the present time, the interpretation of the rate increase due to the added β-methyl groups is speculative and lends no support to the assumption that the partially negative carbonyl oxygen of the carboxyl group attacks the positive sulfur atom with the displacement of a hydroxyl group from the sulfur atom.

The absence of direct iodide ion attack on the protonated sulfoxide species instead of formation of the cyclic intermediate in Allenmark's work can be attributed to the low acid concentrations used to study the reductions. All his

studies were carried out at acid concentrations of 2.0M or lower. Under these conditions, the formation of the cyclic intermediate appears to be favored over direct iodide ion attack on the protonated species.

Landini and co-workers[4] studied the reduction of aryl alkyl and substituted phenyl methyl sulfoxides in aqueous acetic acid containing hydriodic acid and obtained the following information. The reaction is first-order in sulfoxide, second-order in hydriodic acid, and acid catalyzed. The reaction has the following rate equation

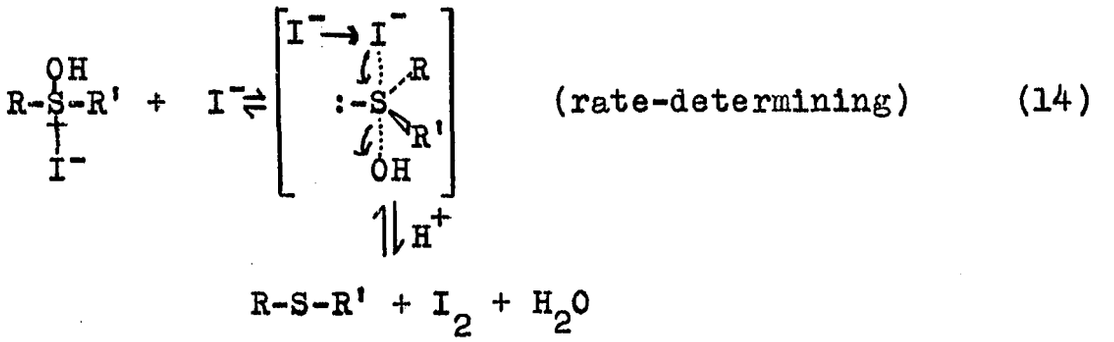
$$\text{rate} = k\,(\text{sulfoxide})\,(HI)^2 \qquad (11)$$

Pseudo-first-order rate constants of the reduction of <u>meta</u>- and <u>para</u>-substituted phenyl methyl sulfoxides fit the Hammett equation[11] giving a $\rho = -0.931$. Studies on the reduction of phenyl methyl, ethyl, isopropyl, and <u>t</u>-butyl sulfoxides indicate that the rate decreases by increasing the size of the alkyl group.

On the basis of the kinetic and stereochemical data the following reaction mechanism was proposed:

$$R\text{-}\overset{\overset{O}{\|}}{S}\text{-}R' + H^+ \rightleftharpoons R\text{-}\overset{\overset{OH}{|}}{\overset{+}{S}}\text{-}R' \quad \text{(equilibrium)} \qquad (12)$$

$$R\text{-}\overset{\overset{OH}{|}}{\overset{+}{S}}\text{-}R' + I^- \rightleftharpoons R\text{-}\overset{\overset{OH}{|}}{\underset{\underset{I^-}{|}}{\overset{+}{S}}}\text{-}R' \qquad (13)$$



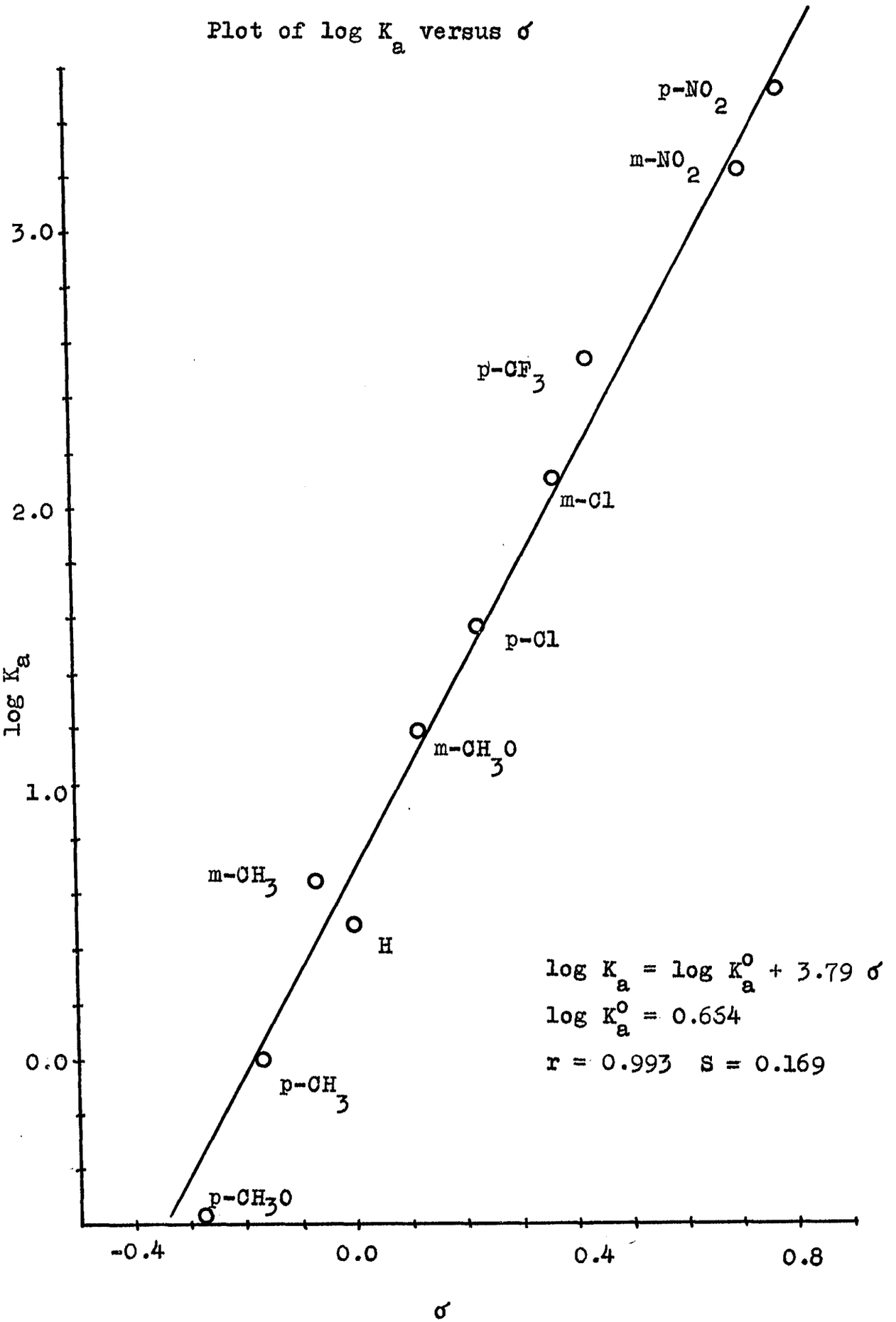
(rate-determining) (14)

$$R\text{-}S\text{-}R' + I_2 + H_2O$$

The slowest step (14) consists of an electron transfer from the iodine to the sulfur promoted by a second iodine ion and an Sn2 type displacement of the -OH group. According to the authors, the negative sign of ρ indicates that the loss of the -OH group precedes the transfer of electrons from the iodine to sulfur. However, they completely neglect the effect of the substituents on the basicity of the sulfoxides. The equilibrium constant for the protonation reaction would depend on the substituents. It has been shown that the apparent pKa's of a series of meta- and para-substituted phenyl methyl sulfoxides give a good Hammett plot with a positive slope[15] as shown in Figure 7. This means that a negative value is to be expected in the iodide reduction reaction, if the effect of the substituent is simply to increase or decrease the concentration of the protonated sulfoxide available for reaction with iodide ion. Based upon this information, Landini and co-workers cannot use the negative sign of ρ as an indication of the substituent effects on the loss of the -OH in the transition state. In order to do this, it would have to be shown that under the conditions used, the sulfoxides were in a completely protonated state. This would eliminate the first step as an equilibrium and nullify the

Figure 7

Plot of log K_a versus σ



substituent effects on the concentration of the protonated species.

Landini determined the second-order dependence on HI by keeping the sulfoxide in excess and observing that the reaction fit a second-order rate expression. Under the conditions used, the HI is completely dissociated into H^+ ions and I^- ions which are most likely acting independently and not as a single molecule of HI. Therefore, in adding a specific concentration of HI, the solution contained equal concentrations of H^+ and I^- ions. Thus, the second-order dependence on HI can be expressed by the following rate expression

$$\text{rate} = k\ (H^+)\ (I^-) \qquad (15)$$

Landini, however, did not vary the H^+ concentration or the I^- concentration in order to determine if the reaction was dependent upon either or both of these ions. Allenmark[7] observed the lack of the dependence of the rate upon I^- ion concentration. If the reaction were independent of I^-, the second-order rate expression could mean that the reaction is second-order with respect to H^+ ion as observed by Krueger.[5]

The kinetic data obtained by Landini and co-workers does not provide enough evidence to support the mechanism proposed which appears to be an attempt at a lucky guess by the authors.

Krueger[5] studied the reduction of dimethyl sulfoxide. The sulfoxide was used as the solvent and aqueous perchloric acid and sodium iodide were added. His study yielded the

following information. The reaction is first-order in iodide ion and second-order in hydrogen ion. Since sulfoxide was in excess, the reaction was found to fit the following rate equation

$$\text{rate} = k\,(H^+)^2(I^-) \qquad (16)$$

The reaction was also catalyzed by chloride ion, bromide ion and thiourea.

Based upon the above information, the following mechanism was proposed for the uncatalyzed reaction.

$$(CH_3)_2SO + H^+ \rightleftharpoons (CH_3)_2SOH^+ \quad \text{(equilibrium)} \qquad (17)$$

$$(CH_3)_2SOH^+ + H^+ \rightleftharpoons (CH_3)_2SOH_2^{2+} \quad \text{(equilibrium)} \qquad (18)$$

$$(CH_3)_2SOH_2^{2+} + I^- \longrightarrow (CH_3)_2SI^+ + H_2O \quad \text{(rate-determining)} \qquad (19)$$

$$(CH_3)_2SI^+ + I^- \longrightarrow (CH_3)_2S + I_2 \qquad (20)$$

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (21)$$

In this mechanism the rate-determining step is the iodide ion displacement of a water molecule from the positive sulfur center. There is no kinetic evidence bearing on equations (20) and (21). They are introduced to indicate a reasonable path leading to the final products. It is pointed out that the attack could occur at oxygen, as well as at sulfur, so that the rate-determining step would become

$$I^- + (CH_3)_2SOH_2^{2+} \longrightarrow (CH_3)_2S + H_2OI^+ \qquad (22)$$

In the case of catalysis by chloride ion, bromide ion and thiourea, the catalytic pathway occurs simultaneously with the direct iodide step. The authors generalize (19) for any nucleophile.

$$N^{n-} + (CH_3)_2SOH_2^2 \longrightarrow (CH_3)_2SN^{2-n} + H_2O \qquad (23)$$

The catalytic effect of the halide ions is attributed to a change in the nucleophilicity of the Cl^-, Br^- and I^- ions in the dimethyl sulfoxide solvent.

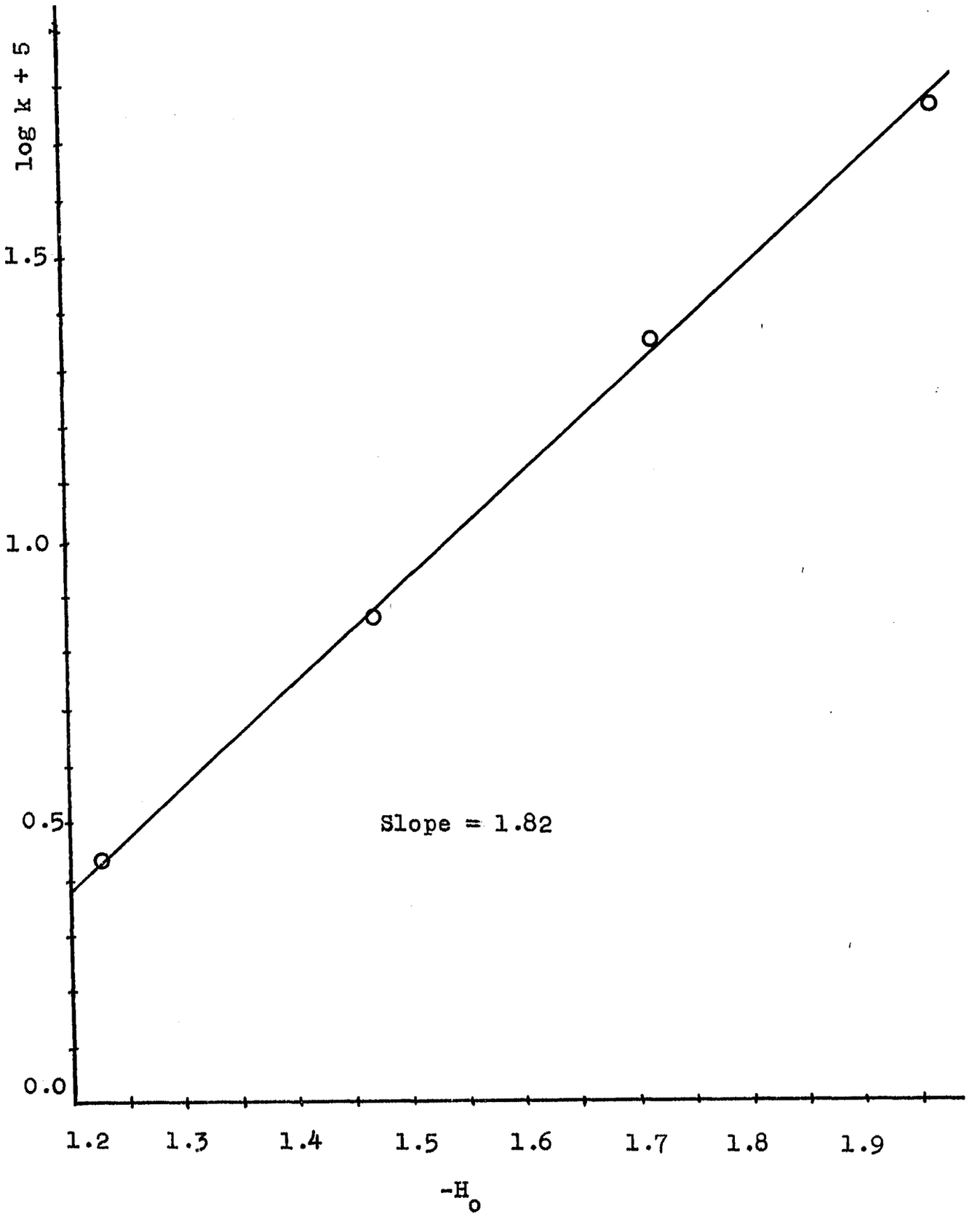
The study of the reduction of aryl alkyl and substituted phenyl methyl sulfoxide in aqueous perchloric acid and sodium iodide presented in this thesis produced the following information. The reduction showed first-order dependence on iodide ion, first-order dependence on sulfoxide, and is acid catalyzed. Under excess acid conditions the reaction fits the following rate equation

$$\text{rate} = k\,(\text{sulfoxide})(I^-) \qquad (24)$$

A plot of log $k_{obs.}$ vs. $-H_o$ resulted in a straight line with a slope of 1.82 as shown in Figure 8. This large value for the slope indicates that the reaction does not appear to follow the general mechanism proposed by Zucker and Hammett for reactions giving a correlation of rate with the acidity function. For reactions known to give a slope of 2 or close to 2, mechanisms have been proposed which indicate the formation of a diprotonated species.[20,21,22] Support for the formation of a diprotonated species in the reduction of the

Figure 8

Plot of log $k_{obs.}$ versus $-H_o$



aryl alkyl and substituted phenyl methyl sulfoxides studied in this work is found in the work of Krueger.[5] His study may be rationalized in terms of a diprotonated sulfoxide species. Assuming diprotonation occurs, if it were possible to carry out the studies presented in this thesis under conditions in which the acid concentration was not in excess, the reaction would most likely show second-order dependence on hydrogen ion and fit the following overall rate equation

$$\text{rate} = k(\text{sulfoxide})(I^-)(H^+)^2 \qquad (25)$$

The reaction is very sensitive to steric effects. Rate studies on phenyl methyl, ethyl, isopropyl, and t-butyl sulfoxides show that increasing the steric bulk of the alkyl group decreases the rate of the reaction. This is what would be expected if the attack of iodide ion is on sulfur in a manner similar to an Sn 2 type substitution on carbon. It is assumed that this is the main effect of the increasing size of the alkyl group. However, other factors can be involved in causing the rate decrease observed. These will be discussed later.

Pseudo-first-order rate constants of the reduction of meta- and para- substituted phenyl methyl sulfoxides fit the Hammett equation giving a $\rho = -0.89$ as illustrated in Figure 4. The negative sign of ρ indicates that the reaction is decreased by electron withdrawing substituents. These substituent effects are in agreement with those observed by Landini.[4]

Based upon the results obtained and the mechanisms proposed in previous studies, a possible mechanism describing the reduction of the sulfoxides in this study is the following:

$$R\text{-}\overset{\overset{O}{\downarrow}}{\underset{\downarrow}{S}}\text{-}R' + H^+ \rightleftharpoons R\text{-}\overset{\overset{OH}{\downarrow}}{\underset{\downarrow}{S}}\text{-}R' \quad \text{(equilibrium)} \tag{26}$$

$$R\text{-}\overset{\overset{OH}{\downarrow}}{\underset{\downarrow}{S}}\text{-}R' + H^+ \rightleftharpoons R\text{-}\overset{\overset{{}^+HOH}{\downarrow}}{\underset{\downarrow}{S}}\text{-}R' \quad \text{(equilibrium)} \tag{27}$$

$$R\text{-}\overset{\overset{{}^+HOH}{\downarrow}}{\underset{+}{S}}\text{-}R' + I^- \longrightarrow R\text{-}\overset{\overset{I}{\downarrow}}{\underset{\downarrow}{S}}\text{-}R' + H_2O \quad \text{(rate-determining)} \tag{28}$$

$$R\text{-}\overset{\overset{I}{\downarrow}}{\underset{\downarrow}{S}}\text{-}R' + I^- \longrightarrow R\text{-}S\text{-}R' + I_2 \tag{29}$$

The rate-determining step can be the displacement of a water molecule similar to the mechanism proposed by Krueger. An alternative possibility for the rate-determining step is that (27) and (28) occur simultaneously in a concerted manner as shown in equation (30).

$$\begin{array}{l} H\text{-}\overset{\overset{H}{\downarrow}}{\underset{\downarrow}{O}}\text{-}H \\ \qquad \alpha\text{-}OH \\ \qquad \alpha^+ R\text{-}S\text{-}R' \\ \qquad \alpha\text{-}I \end{array} \xrightarrow{k_r} R\text{-}\overset{\overset{+}{\downarrow}}{\underset{I}{S}}\text{-}R' + 2H_2O \tag{30}$$

Based upon the information available, the following rate law can be postulated for the rate-determining step of the mechanism:

$$\text{rate} = k_r \left(R\text{-}\overset{\overset{OH}{\downarrow}}{\underset{\downarrow}{S}}\text{-}R'\right)(I^-)(H_3O^+) \tag{31}$$

The concentration of the protonated sulfoxide species can be determined from the following equilibrium:

$$H_2O + R\text{-}\overset{\overset{+}{O}H}{\underset{}{S}}\text{-}R' \quad \underset{}{\overset{K_a}{\rightleftharpoons}} \quad R\text{-}\overset{O}{\underset{}{S}}\text{-}R' + H_3O^+ \tag{32}$$

$$(R\text{-}\overset{\overset{+}{O}H}{\underset{}{S}}\text{-}R') = \frac{(H_3O^+)(R\text{-}\overset{O}{\underset{}{S}}\text{-}R')}{K_a} \tag{33}$$

Substituting into equation (31) results in the following rate expression:

$$\text{rate} = \frac{k_r}{K_a}(R\text{-}\overset{O}{\underset{}{S}}\text{-}R')(I^-)(H_3O^+)^2 \tag{34}$$

Assuming that the first step of the reaction is the only equilibrium and that the rate-determining step is a concerted one as shown in (30), the rate constant for the rate-determining step under pseudo-first-order conditions would be:

$$k_r = \frac{k_{obs.}K_a}{(I^-)(H_3O^+)^2} \tag{35}$$

Since the series of <u>meta</u>- and <u>para</u>-substituted sulfoxides was carried out under pseudo-first-order conditions with the concentration of iodide ion and hydrogen ion held constant, the (I^-) and (H_3O^+) terms can be neglected for the study of the effect of substituents on the rate-determining step of the reaction. This results in the following equation:

$$k_r = k_{obs.}K_a \tag{36}$$

Taking the log of (36) gives the following equation:

$$\log k_r = \log k_{obs.} + \log K_a \qquad (37)$$

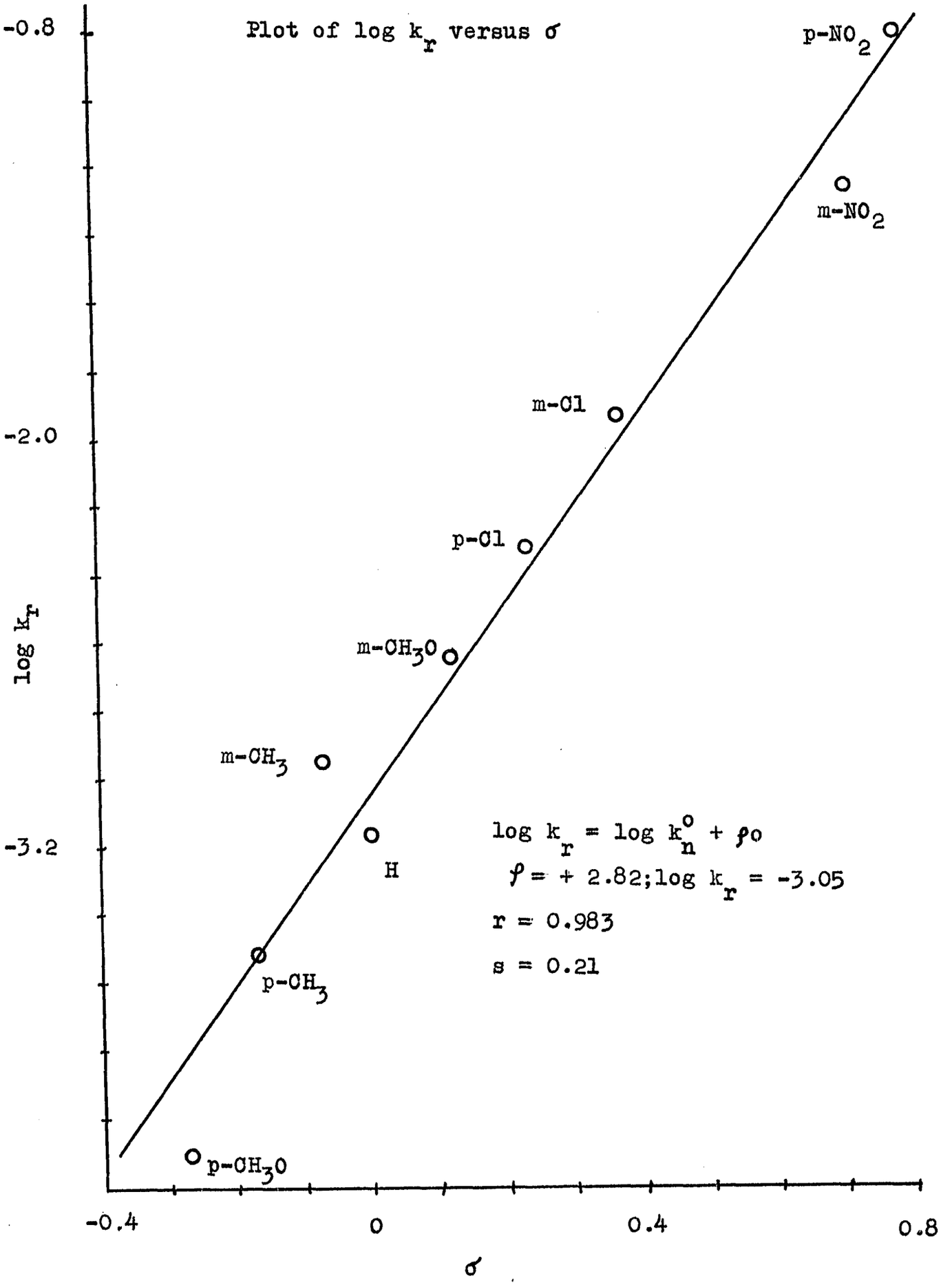
Using the apparent pK_a values determined for the series of meta- and para-substituted phenyl methyl sulfoxides[15] used in this study, a plot of log k_r versus σ^o resulted in a good straight line with $\rho = +2.82$ as shown in Figure 9. This plot should indicate only the effect of substituents upon the transition state, because the substituent effects upon the prior equilibrium step have been accounted for in K_a.

In principle, the rate changes brought about by different substituents should allow an inference concerning the changes in charge density at the reacting center. However, before discussing the significance of the sign of the ρ obtained in the plot of log k_r versus σ^o, it must be remembered that the pK_a's used are only apparent values. They were determined in an acetic acid and acetic anhydride mixture as solvent while the reduction reactions were studied using water as the solvent. Therefore, any interpretation of the data obtained using these values must be considered speculative.

If it is assumed that the pK_a values used are proportional to those for the sulfoxides in the solvent used for studying the reaction, the positive sign of ρ indicates that the amount of positive charge on the reaction center is less in the transition state than in the ground state. Thus, inductively electron-donating groups will cause a decrease in rate. The positive ρ is reasonable for the mechanism postulated

Figure 9

Plot of log k_r versus σ



in this study. In the rate-determining step the reactant molecule is going from a species which has a full positive charge on sulfur in the ground state to a transition state in which the sulfur assumes a partial positive charge with the approach of an I^- ion.

The change in the sign of ρ from negative for the plot of log $k_{obs.}$ to positive for the plot of log k_r would indicate that the substituent effects are operating on the reaction in two distinct ways. In the equilibrium step electron-donating substituents increase the basity of the sulfoxide resulting in the formation of higher concentrations of the protonated sulfoxide species upon which the rate of the reaction is dependent. This increased basicity results in an increase in the rate of the reaction. At the same time, however, electron-donating substituents should decrease the reaction rate due to their effects on the reactive center in the transition state. Based upon the results it would appear that the increase in rate due to substituent effects on the first equilibrium step is greater than the decrease in rate expected from substituent effects on the transition state.

If the preceding interpretation of the data obtained is valid, the positive sign of ρ for the plot of log k_r versus σ^o supports the idea that the iodide ion attacks the positive sulfur with the simultaneous displacement of a leaving group.

As pointed out previously, increasing the size of the alkyl group of the phenyl alkyl sulfoxides caused a decrease in the rate which is assumed to be due mainly to steric effects on the approach of I^- to the sulfur in the rate-determining

step of the reaction.

From the observed rate constants, the following relative rates were obtained: Me(100), Et(60), i-Pr(2.0), t-But(0.04). These relative rates are very similar to those observed by Landini:[4] Me(100), Et(81), i-Pr(1.8), t-But (0.07). Based upon the relative rates observed for Sn2 substitution on sulfur,[46] Me(100), Et(50), i-Pr(0.7), t-Bu(0.0006), the difference between the isopropyl and the t-butyl groups observed in this study is smaller than would be expected if the mechanism for the reduction reaction is also Sn2 substitution on sulfur. The reason for this small change can be explained in two ways.

The first explanation depends upon what effect increasing the size of the alkyl group has on the basicity of the sulfoxide. At present, hydrogen bonding studies indicate that the basicity increases as the size of the alkyl group increases.[47] The apparent pK_a values determined in acetic anhydride by titration with perchloric acid in acetic acid indicates that the basicity decreases as the alkyl group increases in size.[48] These studies are speculative and require further work before any definite conclusions can be made as to which study is giving the correct trend in basicity if there indeed is a change in basicity. These studies point out the fact that the possibility of change in basicity cannot be neglected in the interpretation of changes in rate constants for the phenyl alkyl sulfoxide series.

In order to explain the small change from isopropyl to t-butyl based upon present knowledge of the trends in basicity, it must be assumed that the trend indicated by hydrogen bonding is being followed. As the basicity of the series is increased,

going from methyl to t-butyl, the rate should also be increased due to the effect of increased basicity on the first equilibrium step of the reaction. At the same time, steric effects can be operating on the rate-determining attack of iodide ion on sulfur to decrease the rate. The two effects operating simultaneously could result in the decrease in relative rates between isopropyl and t-butyl.

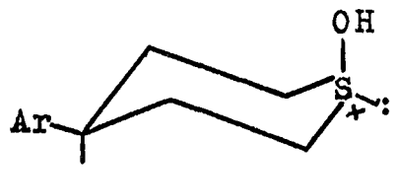
The second explanation depends upon the steric effects of both the alkyl group and the phenyl group upon the reaction. As the alkyl group gets larger, the possibility exists for it to twist the phenyl ring into a position so that it also contributes to the overall steric effect. Based upon this possibility, it can be assumed that for the isopropyl group the steric effect due to it and the phenyl ring is maximized, and the steric effect of the t-butyl group adds relatively little to the rate decrease.

The possibility that the effects given in the preceding explanations are operating at the same time also exists.

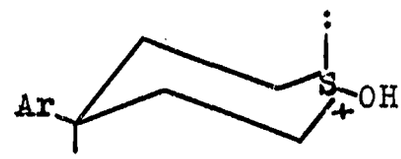
The explanations given are speculative and before any definite conclusions can be made about the steric effects on the reaction, the pK_a values for the sulfoxides must be determined in the solvent system in which the reactions were studied. However, it has been assumed that the decrease in the rate could be due to a combination of the steric effects on the equilibrium step and the rate-determining step but that the primary cause for the overall rate decrease is due to steric effects on the rate-determining step.

In the case of the cis- and trans-4-(4-chlorophenyl)-

thiane-1-oxide, the trans isomer is reduced approximately 24 times faster than the cis isomer. This is opposite to what would be expected if iodide ion is attacking the positive sulfur center and displacing an -OH group in the process according to the mechanism proposed previously. Based upon present theory, a substituent in the axial position on a ring should be displaced more easily because of its higher ground-state energy.[49] This is supported by the fact that cis-4-t-butylcyclohexyl tosylate undergoes displacement with thiophenoxide ion about 19 times faster than the trans isomer. Therefore, if the cis and trans isomers of the thiane-1-oxide studied have the following conformations in the protonated state,



cis

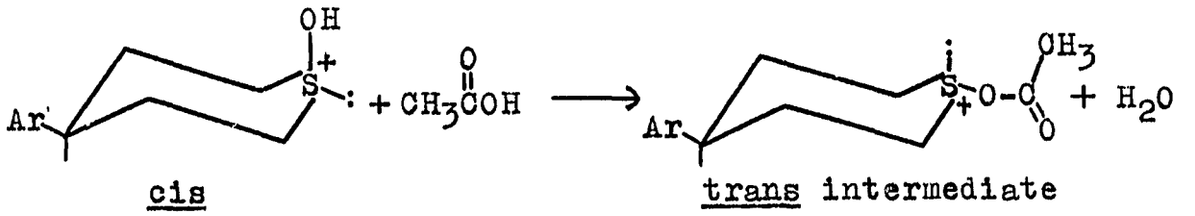


trans

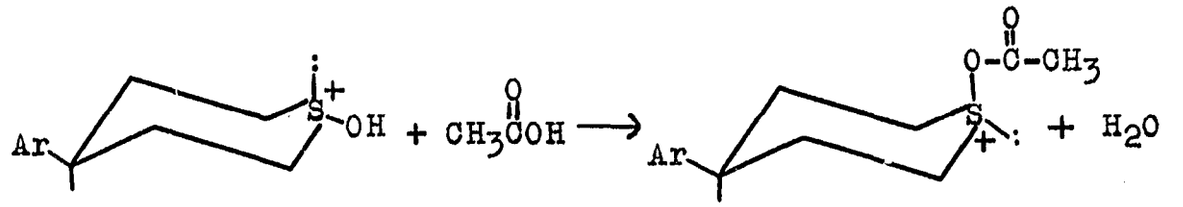
the cis isomer with the axial -OH group would be expected to undergo attack by I^- on the positive sulfur and displace the -OH group much more readily than in the trans isomer.

A possible explanation for the trans isomer reacting faster than the cis is that the solvent has an effect on the reaction. The reaction was studied in a solvent of 50% water and 50% acetic acid by volume with the acid concentration at 4.0M and the iodide ion concentration at 0.2M. It was found by Allenmark[6-9] that a carboxyl group on the substrate is most likely involved in the reduction of the sulfoxides studied.

Therefore, if this is possible in Allenmark's case, it may also be possible for cases where the carboxyl group can come from the solvent instead of being directly connected to the reacting molecule. Using the assumption that the acetic acid from the solvent is involved in the reduction of the cis- and trans-4-(4-chlorophenyl)-thiane-1-oxide in the same manner as shown previously in Figure 6 for Allenmark's studies, the following intermediates can be proposed as resulting from the attack of acetic acid on the sulfur with the loss of the -OH group.



cis trans intermediate



trans cis intermediate

If these intermediates are formed prior to the attack of I^- on sulfur, the cis isomer has now been converted to an intermediate with a substituent on sulfur in the equatorial position, and the trans isomer is converted to an intermediate with a substituent on sulfur in the axial position. Following present theory, the intermediate formed from the trans isomer should react faster than the intermediate from the cis isomer.

This would be in agreement with the results obtained.

Also, if present theory is correct, the formation of the intermediates proposed cannot be rate-determining. If it were, the cis isomer would be expected to react faster than the trans. The rate-determining step is most likely the attack of I^- on the intermediates formed after attack by acetic acid.

The explanation for the results obtained for the cis- and trans-4-(4-chlorophenyl)-thiane-1-oxide in this study is reasonable based upon available information, but until more evidence is found substantiating the existence of the proposed intermediates, it is speculative.

EXPERIMENTAL

Materials

Thiophenols

p-Toluenethiol, p-chlorothiophenol and thiophenol were commerically available. All others used were synthesized.

p-Nitrothiophenol. This thiophenol was prepared according to the procedure of Price and Stacy.[23] A 1-liter three-necked flask was fitted with a stirrer, reflux condenser, and a dropping funnel. A solution of sodium disulfide prepared from sodium sulfide (175 g., 0.720 moles) and sulfur (23.4 g., 0.720 moles) in 150 ml. of 95% ethanol was added in small portions over a period of 10 min. to a solution of p-nitrochlorobenzene (157.5 g., 1.00 moles) in 250 ml. of 95% ethanol. The solution was brought to reflux temperature, and an alcoholic solution of sodium hydroxide (40 g., 1.00 moles) was added dropwise over a period of about 20 min. while the solution was refluxing. After refluxing for a total time of 45 min., the mixture was cooled and then poured onto 1 kg. of ice and 1 liter of water. A precipitate was removed by filtration. The filtrate was acidified with hydrochloric acid, and the p-nitrothiophenol collected

by filtration and washed with 500 ml. of water. The crude product was dissolved in 150 ml. of 95% ethanol. This was then added to 1 liter of 1 M sodium hydroxide. The solution was filtered, and the filtrate was again acidified as before. The product was collected by filtration and used in the crude form (55.8 g., 0.360 moles, 50% yield).

p-Methoxythiophenol. This thiophenol was prepared according to the procedure in Organic Syntheses for thiophenol.[24] A 5-liter three-necked flask was fitted with a reflux condenser, thermometer, and stirrer. Then 3 kg. of crushed ice and 600 ml. of conc. sulfuric acid was added to the flask. The mixture was cooled to below -5° in a Dry Ice and acetone bath while stirring. p-Methoxybenzenesulfonyl chloride (206 g., 1.00 mole) was gradually added. Zinc dust (500 g., 7.65 moles) was added in small portions as rapidly as possible without allowing the temperature to rise above -5°. The contents of the flask were stirred for about 1½ hr. longer at this temperature. After this time, the flask was warmed by heating gently with a burner. Within a few minutes, a rather vigorous reaction occurred, and the flask was cooled under a stream of cold water. After this first reaction, the mixture was heated to boiling and refluxed for about 6 hr. The p-methoxythiophenol was then steam distilled. The thiol was taken up in chloroform and dried over anhydrous magnesium sulfate. This was filtered, and the chloroform removed under vacuum. The residual oil was distilled through a 15 cm. Vigreux column. The main

fraction distilled at 53-54° (0.2 mm.), lit.[25] b.p. 89-90° (5 mm.), (112 g., 0.800 mole, 80% yield). (Infrared spectrum no. 2600)

m-Chlorothiophenol. A 2-liter beaker equipped with a stirrer and thermometer was immersed in an ice and salt bath. Hydrochloric acid (150 ml., conc.) and m-chloroaniline (95.7 g., 0.750 mole) were added to the beaker, and crushed ice (150 g.) was added to cool the mixture. This was cooled to 0° and a cold solution of sodium nitrite (55 g., 0.800 mole) in 125 ml. of water was added dropwise keeping the temperature always below 4°.

In another 2-liter beaker equipped with a thermometer, dropping funnel, and stirrer, potassium ethyl xanthate (140 g., 0.880 mole) was dissolved in 180 ml. of water. The solution was warmed to 40-45° and kept in that range during the slow addition of the cold diazonium solution. The dianzonium solution was kept in the ice bath, and only small portions were placed in the dropping funnel at one time. About 2 hr. were required. After an additional 30 min. at this temperature to insure complete decomposition of the intermediate compound, the dark red oily xanthate was separated. The aqueous layer was extracted twice using 100 ml. portions of ether. The combined oil and ether extracts were washed once with 100 ml. of 10% sodium hydroxide and then with several portions of water until the washings were neutral to litmus. The ether solution was dried over anhydrous

magnesium sulfate and filtered. The ether was removed under vacuum. The crude xanthate was added to a 1-liter three-necked flask fitted with a reflux condenser and containing 500 ml. of 95% ethanol. This solution was brought to boiling and the source of heat removed. While still hot, potassium hydroxide pellets (175 g., 3.00 moles) were added slowly to keep the solution boiling. The mixture was then refluxed for 8 hr. after which approximately 400 ml. of the ethanol was removed by distillation on a steam bath. The residue was taken up in a minimum amount of water, about 500 ml. This solution was made strongly acid to Congo Red paper by adding 6N sulfuric acid. The resulting solution was extracted with chloroform. The chloroform solution was dried over anhydrous magnesium sulfate and filtered. The chloroform was removed under vacuum, and the residual dark brown oil was distilled through a 15 cm. Vigreux column. The main fraction distilled at 52-54° (0.8 mm.), lit.[26] b.p. 90-92° (13 mm.), (72 g., 0.500 mole, 50% yield). (Infrared spectrum no. 2445)

m-Toluenethiol and m-Methoxythiophenol. These thiophenols were prepared in the same manner as the m-chlorothiophenol. m-Toluidine and m-anisidine were used, respectively.

m-Toluenethiol distilled at 147° (80 mm.), lit.[27] b.p. 90-93° (25 mm.), (68.2 g., 0.550 mole, 73% yield). (Infrared spectrum no. 2994)

m-Methoxythiophenol distilled at 62-63° (0.5 mm.), lit.[28] b.p. 78° (4 mm.), (29.4 g., 0.210 mole, 28% yield). (Infrared spectrum no. 2583)

m-Nitrothiophenol. This particular thiol was not isolated, but was prepared as its sodium salt in the following manner. Sodium sulfide (43.6 g., 0.290 mole, 60% assay) was placed in a 1-liter one-neck flask containing 300 ml. of methanol. This mixture was stirred magnetically. When the sodium sulfide had dissolved completely, the solution was covered with a nitrogen atmosphere. A hot solution of 300 ml. of methanol containing m-nitrophenyl disulfide (88.4 g., 0.290 mole) was added to this solution. As the hot alcohol solution was added under a stream of nitrogen, the solution became dark red in color. The change in color indicated the formation of the sodium salt of m-nitrothiophenol. This salt solution was used to prepare the methyl sulfide.

Sulfides

The sulfides given in Table 8 were prepared by alkylating the appropriate thiophenols with dimethyl sulfate according to the general procedure given on the following page.

Table 8

Substituted Phenyl Methyl Sulfides

X-ArSCH$_3$	B.p./mm. Hg - M.p. (Solvent)	Ref.
p-CH$_3$	62-63 (0.25 mm.)	(29)
m-CH$_3$	56-57 (0.6 mm.)	(29)
p-CH$_3$O	53-54 (0.2 mm.)	(29)
m-CH$_3$O	61-62 (0.2 mm.)	(30)
p-Cl	134-136 (5 mm.)	(29)
m-Cl	60-61 (0.6 mm.)	(29)
p-NO$_2$	71-72 (ligrion)	(29)
H	76-77 (10 mm.)	(31)

The thiophenol (0.50 mole) was placed in a 500 ml. Erlenmyer flask, and sodium hydroxide (0.80 mole) in 200 ml. of water was added. The flask was cooled in an ice bath, and dimethyl sulfate (0.70 mole) was added dropwise while the solution was stirred magnetically. After addition of the dimethyl sulfate, the solution was allowed to stir while coming to room temperature. The solution either separated into two layers or a solid precipitated out. In the case of the oily layer, this was separated, and the aqueous layer extracted with ether. The oil and ether extracts were combined, dried over anhydrous magnesium sulfate, and filtered. The ether was removed under vacuum, and the residual oil was fractionally distilled through a 15 cm. Vigreux column. In the case of the solid precipitate, this was collected and recrystallized from the appropriate solvent. The yields were 85-90%.

m-Nitrophenyl Methyl Sulfide. The sodium m-nitrothiophenolate prepared previously was made basic by adding 100 ml. of methanol saturated with sodium hydroxide. This was done under a nitrogen atmosphere. Dimethyl sulfate (75 ml., 0.790 mole) was added to the solution. It turned a light yellow, and a light yellow solid formed. The solid was filtered off and added to water. It dissolved; the solution was extracted with ether. The alcohol solution was diluted with water and extracted with ether. The ether layers were combined, dried over anhydrous magnesium sulfate, and filtered. The ether was removed under vacuum, and the residual oil was distilled through a 15 cm. Vigreux column. The main fraction distilled at 87-88° (0.15 mm.), lit.[32] b.p. 133-134° (4 mm.), (81 g., 0.480 mole, 80% yield).

Phenyl Ethyl Sulfide. Ethyl bromide (109 g., 1.00 mole) was added dropwise to 250 ml. of water containing sodium hydroxide (50 g.) and thiophenol (102 ml., 1.00 mole). The solution was cooled in an ice bath and stirred magnetically. The solution was allowed to warm up to room temperature and stirred for two days. The top layer was separated and the aqueous layer extracted with ether. The oily layer and the ether extracts were combined, dried over anhydrous magnesium sulfate and filtered. The ether was removed under vacuum, and the residual oil was distilled through a 15 cm. Vigreux column. The main fraction distilled at 54-55° (1 mm.), lit.[31] b.p. 86-87° (13 mm.), (110 g., 0.800 mole, 80% yield)

4-(p-Chlorophenyl)-Thiane. This sulfide was prepared by the synthetic procedures outlined below.

a) Ethyl 3-(p-Chlorophenyl)-3-Hydroxypropionate. A 1-liter three-necked flask fitted with a mechanical stirrer, reflux condenser, and addition funnel was flushed with dry nitrogen and charged with zinc dust (80 g., 1.20 mole). A solution of ethyl bromoacetate (111 ml., 1.0 mole), p-chlorobenzaldehyde (171 g., 1.20 mole), dry benzene (160 ml.), and dry ether (40 ml.) was placed in the addition funnel; about 10 ml. of the solution was added to start the reaction. If the reaction did not start, heat was applied so the solution refluxed. Once reaction had started, stirring was begun, and the solution added dropwise so that the mixture refluxed gently. After addition was complete, heat was applied, and the mixture refluxed for an additional hour. The flask was cooled, and 400 ml. of 10% sulfuric acid was added. The mixture separated into two layers. The top ether layer was removed, and the lower aqueous acid layer was extracted with ether. The ether layers were combined, washed with 10% sodium carbonate, water, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the remaining oil was distilled through a 15 cm. Vigreux column. The main fraction distilled at 140° (0.8 mm.), (137 g., 0.60 mole, 60% yield). (Infrared spectrum no. 4010)

b) Ethyl p-Chlorocinnamate. Ethyl-3-(p-chlorophenyl)-3-hydroxypropionate (137 g., 0.60 mole) was placed in a 500-ml. one-neck flask and 200 ml. of acetic anhydride added. The

mixture was refluxed for 1 hr., and the acetic anhydride-acetic acid mixture was distilled off. This mixture distilled between 135-145°. The dehydration was complete when the mixture was completely distilled over, and the temperature dropped below 100°. The remaining liquid was distilled under vacuum through a 15 cm. Vigreux column. The main fraction distilled at 100-101° (0.3 mm.), lit.[33] b.p. 160° (11 mm.), (105 g., 0.50 mole, 83% yield). (Infrared spectrum no. 4038)

c) β-(p-Chlorophenyl)-Glutaric Acid. A 1-liter three-necked flask fitted with a reflux condenser, stirrer, and dropping funnel was flushed with nitrogen and charged with super-dry absolute ethanol (253 ml., 4.3 moles) and clean sodium (18.4 g., 0.80 mole). After the sodium had reacted completely, the flask was cooled, and redistilled diethyl malonate (151 ml., 1.0 mole) was added to the flask through the condenser while the contents of the flask were being stirred. A paste-like solid formed upon addition of the diethyl malonate. The flask was heated, and the solid dissolved. When the mixture was refluxing gently, ethyl p-chlorocinnamate (120.5 g., 0.57 mole) was added dropwise. The solution was refluxed for an additional hour. The flask was cooled, and glacial acetic acid (47.5 ml., 0.83 mole) was added. Excess alcohol was removed by distillation under reduced pressure. Enough water was added to dissolve all the solid material. The ester layer was separated, and the aqueous

layer extracted with four 25-ml. portions of carbon tetrachloride. The combined ester and carbon tetrachloride extracts were washed twice with 25-ml. portions of water. The solution was dried over anhydrous sodium sulfate, and the carbon tetrachloride removed under vacuum. The residual oil was distilled through a 15 cm. Vigreux column. The main fraction distilled at 170-171° (0.6 mm.).

The product was placed in a 500-ml. one-neck flask which was stirred magnetically and fitted with a reflux condenser. Concentrated hydrochloric acid (200 ml.) was added, and the mixture refluxed for about 8 hr. The acid solution was decanted, and the process repeated until crystalline product remained in the flask. The β-(p-chlorophenyl)-glutaric acid was collected, washed with water, and air dried. The crude material melted at 161-164°, lit.[34] m.p. 164-165°, (101 g., 0.46 mole, 80% yield based on ethyl p-chlorocinnamate).

d) Ethyl β-(p-Chlorophenyl)-Glutarate. A 500-ml. one-neck flask fitted with a condenser and stirred magnetically was charged with β-(p-chlorophenyl)-glutaric acid (101 g., 0.46 mole), absolute ethanol (268 ml., 4.60 moles), and concentrated sulfuric (11.6 ml., 0.22 mole). The mixture was refluxed for 4 hr. The flask was cooled, and the contents poured into water. The product separated as a light yellow oil. The water solution was extracted with ether, and the extracts and ester were combined and dried over anhydrous

sodium sulfate. The ether was removed under vacuum, and the residual oil distilled through a 15 cm. Vigreux column. The main fraction distilled at 139-140° (0.3 mm.), lit.[34] b.p. 151-161° (1-1.7 mm.), (91.1 g., 0.30 mole, 70% yield). (Infrared spectrum no. 4115)

e) 3-(4-Chlorophenyl)-1,5-Dihydroxypentane. A 2-liter three-necked flask fitted with a reflux condenser, stirrer and addition funnel was charged with 1 liter of anhydrous ether and powdered lithium aluminum hydride (23 g., 0.60 mole). Ethyl β-(p-chlorophenyl)-glutarate (179 g., 0.60 mole) in 500 ml. of dry ether was added dropwise so that the solution refluxed gently. After addition was complete, the solution was stirred for an additional half hour. Dilute hydrochloric acid was added to hydrolyze the mixture. The mixture was stirred until there were two clear liquid phases. The top ether layer was separated, washed with 10% sodium carbonate, water and dried over anhydrous magnesium sulfate. The ether was removed under vacuum, and the residual oil was distilled through a 15 cm. Vigreux column. The main fraction distilled at 170-171° (0.7 mm.), lit.[34] b.p. 166° (0.8 mm.), (85.6 g., 0.40 mole, 65% yield) (Infrared spectrum no. 4130)

f) 3-(4-Chlorophenyl)-1,5-Dibromopentane. This dibromide was prepared according to the procedure of Allinger and Greenberg.[34] 3-(4-Chlorophenyl)-1,5-dihydroxypentane (85.6 g., 0.46 mole) was placed in a 250-ml. three-necked flask fitted with a thermometer, gas outlet tube, a gas inlet tube,

and stirred magnetically. The flask was heated to 130°, and anhydrous hydrogen bromide was passed into it for about 8 hr. The reaction mixture turned a real dark brown, and was taken up in ether. The ether solution was washed with 5% sodium carbonate solution, water, and dried over anhydrous sodium sulfate. The ether was removed under vacuum, and the residual oil was distilled through a 15 cm. Vigreux column. The main fraction distilled at 96° (0.6 mm.), and a second smaller fraction distilled at 153-154° (0.4 mm.).

The compound obtained at 96° was not the dibromide. Based upon the conditions of the reaction, infrared spectrum, and nuclear magnetic resonance spectrum, it was assumed that the product was 4-(4-chlorophenyl)-pyran. It was refluxed with 57% hydriodic acid for about 8 hr. The resulting mixture was taken up in ether and washed with a dilute solution of sodium bisulfite to remove iodine. The ether layer was washed with water several times, dried over anhydrous magnesium sulfate and filtered. The ether was removed under vacuum, and the residual oil was added to a solution of sodium sulfide in 95% ethanol with stirring. Heat was evolved indicating a reaction. The mixture was stirred for about 2 hr., and then water was added to the alcohol. A light yellow oil came out of solution. This was separated off, and the solution extracted with ether. The oil and ether extracts were combined, dried over anhydrous magnesium sulfate, and filtered. The ether was removed under vacuum, and the remaining oil was boiled with low boiling petroleum ether. The

petroleum ether was decanted and cooled. Upon cooling 4-(4-chlorophenyl)-thiane began to crystallize.

The second fraction, b.p. 153-154° (0.4 mm.), was 3-(4-chlorophenyl)-1,5-dibromopentane, lit.[34] b.p. 192-194° (7 mm.), (71.4 g., 0.21 mole, 46% yield). (Infrared spectrum no. 4168)

g) 4-(4-Chlorophenyl)-Thiane. This sulfide was prepared according to the procedure of Johnson.[35] 3-(4-Chlorophenyl)-1,5-dibromopentane (71.4 g., 0.21 mole) was added slowly to a 1 liter beaker containing 500 ml. of 95% ethanol and sodium sulfide (50.4 g., 0.21 mole). Heat was generated as the dibromide was added. The mixture was allowed to stir for several hours. Upon cooling, crystals came out of solution. These were collected, washed with water, and air dried, m.p. 69-70° (ethanol), lit.[35] m.p. 70-71° (petroleum ether), (37 g., 0.17 mole, 80% yield). (Infrared spectrum no. 4420)

Sulfoxides

Phenyl Methyl Sulfoxide. Phenyl methyl sulfide (62 g., 0.50 mole) was added to 200 ml. of glacial acetic acid in a 500 ml. Erlenmeyer flask which was cooled in an ice bath and stirred magnetically. Hydrogen peroxide (30%, 57 ml., 0.50 mole) was added dropwise to this solution. The flask was kept at 10° for 2 days and allowed to stand at room temperature for an additional day. The solvent was removed under vacuum, and the remaining oil washed with 5% sodium carbonate. The oil was taken up in ether, dried over

anhydrous magnesium sulfate, and filtered. The ether was removed under vacuum, and the remaining oil dried over Linde 13X molecular seives. The oil was distilled from the seives through a 15 cm. Vigreux column. The main fraction distilled at 94-95° (1.0 mm.), lit.[36] b.p. 144° (15 mm.), (40 g., 0.285 mole, 57% yield). (Infrared spectrum no. 280)

Phenyl Ethyl Sulfoxide. Phenyl ethyl sulfide (74 g., 0.50 mole) was added to 250 ml. of methanol in a 500 ml. one-neck flask which was cooled in a Dry Ice and acetone bath and stirred magnetically. t-Butyl hypochlorite[37] (54 g., 0.50 mole) was added dropwise. The flask was allowed to warm up to room temperature, and the solvent was removed under vacuum. The residual oil was washed with 5% sodium carbonate and taken up in ether. The ether solution was dried over anhydrous magnesium sulfate and filtered. The ether was removed under vacuum, and the remaining oil was dried over Linde 13X molecular seives. The oil was distilled from the seives through a 15 cm. Vigreux column. The main fraction distilled at 91-92° (0.5 mm.), lit.[38] b.p. 101-102° (1 mm.), (46.3 g., 0.30 mole, 60% yield). (Infrared spectrum no. 893)

Phenyl Isopropyl Sulfoxide. A 1-liter three-necked flask was fitted with a reflux condenser and dropping funnel. Magnesium turnings (14.6 g., 0.60 mole) and 500 ml. of anhydrous ether were added to the flask and stirred magnetically. Isopropyl bromide (57 ml., 0.60 mole) was added dropwise.

A 2-liter three-necked flask was fitted with a stirrer,

dropping funnel, and drying tube. Methyl benzenesulfinate[39] (92.5 g., 0.620 mole) and 500 ml. of anhydrous ether were added to the flask which was cooled in an ice bath. The Grignard reagent was added dropwise while the ester solution was stirred vigorously. The solution was hydrolyzed with saturated ammonium chloride solution until large lumps of precipitate formed. The clear ether layer was decanted, and the precipitate dissolved in water. The water solution was extracted with ether. The ether layers were combined, and the ether removed under vacuum. The remaining oil was added to a beaker containing 150 ml. of 35% perchloric acid. It was completely soluble in this solution which was then extracted with carbon tetrachloride. Upon adding the carbon tetrachloride and extracting, an oily layer separated out on top of the acid solution. This layer was separated, and upon neutralizing in sodium carbonate solution, it went into solution completely. It was forced out of solution by saturation of the solution with sodium chloride. The solution was extracted with chloroform. This was dried over anhydrous magnesium sulfate and filtered. The chloroform was removed under vacuum, and the residual oil distilled without column. The main fraction distilled at 85-86° (0.25 mm.), lit.[40] b.p. 127° (7 mm.), (29.4 g., 0.174 mole, 35% yield). (Infrared spectrum no. 3904)

Phenyl t-Butyl Sulfoxide. A 1-liter three-necked flask was fitted with a reflux condenser and dropping funnel. Magnesium turnings (7.3 g., 0.30 mole) and 250 ml. of anhydrous

ether were added to the flask and stirred magnetically. t-Butyl chloride (32.8 ml., 0.30 mole) was added dropwise.

A 1-liter three-necked flask was fitted with a stirrer, dropping funnel, and drying tube. Methyl benzenesulfinate (48 g., 0.30 mole) and 300 ml. of anhydrous ether were added to the flask which was cooled in an ice bath. The Grignard reagent was added dropwise while the ester solution was stirred vigorously. The solution was hydrolyzed with saturated ammonium chloride solution until large lumps of precipitate dissolved in water. The water solution was extracted with ether. The ether layers were combined, and the ether was removed under vacuum. The remaining oil was added to a beaker containing 150 ml. of 35% perchloric acid. It was completely soluble in this solution which was then extracted with carbon tetrachloride. Upon adding the carbon tetrachloride and extracting, an oily layer separated out on top of the acid solution. This layer was separated, and upon neutralizing in sodium carbonate solution, it went into solution completely. It was forced out of solution by saturation with sodium chloride. The solution was extracted with chloroform. This was dried over anhydrous magnesium sulfate and filtered. The chloroform was removed under vacuum, and the residual oil was boiled with low boiling petroleum ether. The sulfoxide was recrystallized from petroleum ether; m.p. 56.5-57.5°, lit.[40] m.p. 58-59° (ethanol), (22 g., 0.120 mole, 40% yield). (Infrared spectrum no. 3905)

p-Nitrophenyl Methyl Sulfoxide. p-Nitrophenyl methyl

sulfide (42.2 g., 0.25 mole) and 300 ml. of methanol were added to a 1-liter one-neck flask which was cooled in an ice bath and stirred magnetically. The sulfide did not go into solution completely. t-Butyl hypochlorite (27 g., 0.250 mole) was added dropwise to the reaction flask. The reaction mixture turned a dark brown color upon addition of the t-butyl hypochlorite. By the end of the addition, the solution was completely homogeneous. The reaction flask was allowed to come to room temperature while stirring for about 4 hr. During this time, crystals came out of solution. They were collected and air dried. The crystals were light brown in color. These were then decolorized using Norit and recrystallized from 95% ethanol. The final product was light yellow; m.p. 148-149°, lit.[41] m.p. 149° (ethanol), (25.4 g., 0.150 mole, 60% yield). (Infrared spectrum no. 915)

p-Tolyl Methyl Sulfoxide. p-Tolyl methyl sulfide (50.5 g., 0.37 mole) was added to 250 ml. of methanol in a 500 ml. one-neck flask which was cooled in an ice bath and stirred magnetically. t-Butyl hypochlorite (38 g., 0.520 mole) was added to the reaction flask dropwise. After addition of the t-butyl hypochlorite, the reaction flask was allowed to warm up to room temperature. The solvent was reduced to a volume of 100 ml. Then 5% sodium carbonate (150 ml.) was added to the flask, and an oil separated out. The oil was taken up in ether, dried over anhydrous magnesium sulfate and filtered. The ether was removed under vacuum, and the remaining oil was dried over Linde 13X molecular seives.

The oil was distilled from the seives through a 15 cm. Vigreux column. The main fraction distilled at 92-93° (0.2 mm.), m.p. 42-43° (ether), lit.[41] m.p. 43-44° (ether), (20 g., 0.129 mole, 35% yield). (Infrared spectrum no 914)

p-Methoxyphenyl Methyl Sulfoxide. p-Methoxythioanisole (38.5 g., 0.25 mole) was added to 500 ml. of methanol in a 1-liter one-neck flask which was cooled in an acetone-Dry Ice bath and stirred magnetically. t-Butyl hypochlorite (27 g., 0.250 mole) was added dropwise from a dropping funnel. After addition was complete, the solution was allowed to warm up, and at -40° some sodium carbonate was added to the flask. Upon reaching room temperature, the methanol was removed under vacuum. Ether was added to the residual oil and solid remaining in the flask. This solution was dried over anhydrous magnesium sulfate and filtered. The ether was removed under vacuum, and the remaining oil was dried over Linde 13X molecular seives. The oil was distilled from the seives through a 15 cm. Vigreux column. The main fraction distilled at 122-123° (0.25 mm.), lit.[41] b.p. 153-154° (5 mm.), (32 g., 0.188 mole, 75% yield). (Infrared spectrum no. 2657)

p-Chlorophenyl Methyl Sulfoxide. p-Chlorophenyl methyl sulfide (39.6 g., 0.250 mole) was added to 500 ml. of methanol in a 1-liter one-neck flask which was cooled in an acetone-Dry Ice bath and stirred magnetically. t-Butyl hypochlorite (27 g., 0.250 mole) was added dropwise from a dropping funnel. After addition was complete, the solution was allowed to warm up, and at -40° some sodium carbonate was

added to the flask. Upon reaching room temperature, the methanol was removed under vacuum. Ether was added to the residual oil and solid remaining in the flask. This solution was dried over anhydrous magnesium sulfate and filtered. The ether was removed under vacuum, and the remaining oil was dried over Linde 13X molecular seives. The oil was distilled from the seives through a 15 cm. Vigreux column. The main fraction distilled at 94-100° (0.05 mm.), and crystallized upon standing. The sulfoxide was recrystallized from ether; m.p. 46-47°, lit.[41] m.p. 47-48° (ether), b.p. 135-136° (5 mm.), (25.3 g., 0.145 mole, 58% yield).

m-Chlorophenyl Methyl Sulfoxide. m-Chlorophenyl methyl sulfide (56.7 g., 0.360 mole) was added to 500 ml. of methanol in a 1-liter one-neck flask which was cooled in an acetone-Dry Ice bath and stirred magnetically. t-Butyl hypochlorite (38 g., 0.360 mole) was added dropwise from a dropping funnel. After addition of the hypochlorite, the solution was allowed to warm up, and at -40° sodium carbonate was added. Upon reaching room temperature, the methanol was removed under vacuum. The residual oil and some excess sodium carbonate were taken up in ether, dried over anhydrous magnesium sulfate, and filtered. The ether was removed under vacuum, and the remaining oil was dried over Linde 13X molecular seives. The oil was distilled through a 15 cm. Vigreux column. The main fraction distilled at 125-126° (1.3 mm.), lit.[41] b.p. 100-101° (0.10 mm.), (30 g., 0.114 mole, 32% yield). (Infrared spectrum no. 2562)

m-Tolyl Methyl Sulfoxide. m-Tolyl methyl sulfide

(59 g., 0.430 mole) was added to 500 ml. of methanol in a 1-liter one-neck flask which was cooled in an acetone-Dry Ice bath and stirred magnetically. t-Butyl hypochlorite (46.5 g., 0.430 mole) was added dropwise from a dropping funnel. After addition of the hypochlorite, the same procedure was followed as for the m-methoxyphenyl methyl sulfoxide. The main fraction distilled at 94° (0.35 mm.), lit.[41] b.p. 126-127° (3 mm.), (25 g., 0.162 mole, 38% yield). (Infrared spectrum no. 3754)

m-Nitrophenyl Methyl Sulfoxide. m-Nitrophenyl methyl sulfide (43.5 g., 0.250 mole) was added to 500 ml. of methanol in a 1-liter one-neck flask which was cooled in an acetone-Dry Ice bath and stirred magnetically. The sulfide crystallized out of the alcohol upon cooling. t-Butyl hypochlorite (27 g., 0.250 mole) was added dropwise from a dropping funnel. After the addition, the flask was allowed to come to room temperature. Then sodium carbonate was added, and the methanol was reduced in volume under vacuum. The volume was taken down to 100 ml., and the methanol was then heated to boiling and filtered to remove the insoluble salts. The sulfoxide crystallized out of the hot alcohol solution upon cooling. The sulfoxide was collected and recrystallized several times from 95% ethanol; m.p. 115-116°, lit.[41] m.p. 117-118° (ethanol), (25 g., 0.135 mole, 54% yield). (Infrared spectrum no. 3384)

m-Methoxyphenyl Methyl Sulfoxide. m-Methoxyphenyl methyl sulfide (32.4 g., 0.210 mole) was added to 500 ml. of methanol in a 1-liter one-neck flask which was cooled in an acetone-Dry Ice bath and stirred magnetically. t-Butyl

hypochlorite (22.7 g., 0.210 mole) was added dropwise. After addition was complete, the solution was allowed to warm up, and at -40° sodium carbonate was added. Upon reaching room temperature, the methanol was removed under vacuum, and the residual oil taken up in ether. This solution was dried over anhydrous magnesium sulfate and filtered. The ether was removed under vacuum, and the residual oil was added to 100 ml. of 35% perchloric acid. This solution was extracted with carbon tetrachloride, and the acid solution was neutralized with sodium carbonate. The solution was then saturated with sodium chloride, and the sulfoxide was separated from the solution. The solution was extracted with chloroform, and the extracts were combined with the sulfoxide. The solution was dried over anhydrous magnesium sulfate and filtered. The chloroform was removed under vacuum, and the residual oil was dried over Linde 13X molecular seives. The sulfoxide was distilled from the seives without a column. The main fraction distilled at 103-104° (0.20 mm.), lit.[42] b.p. 125-127° (16-17 mm.), (15 g., 0.088 mole, 42% yield). (Infrared spectrum no. 2592)

cis-4-(4-Chlorophenyl)-Thiane-1-Oxide. This sulfoxide was prepared according to the procedure given by Johnson and McCants.[43] A 1-liter one-neck flask was filled with 500 ml. of methanol and 4-(4-chlorophenyl)-thiane (16 g., 0.075 mole). The flask was cooled in a Dry Ice and acetone bath while being stirred magnetically. Upon cooling the sulfide crystallized out of the methanol. t-Butyl hypochlorite (8.64 g., 0.08 mole)

was added dropwise. The sulfide gradually went into solution as the t-butyl hypochlorite was added, and it was stirred for an additional half hour. The solution was allowed to warm up, and at about -40° anhydrous sodium carbonate (2 g.) was added. The mixture was stirred until it reached room temperature. The solid remaining was filtered off, and the alcohol removed under vacuum. As the volume of the methanol was reduced more solid came out of solution. The volume was reduced to about 150 ml., and the solid removed by filtration. The methanol was again reduced in volume until a thick paste-like solid remained. This was added to 200 ml. of ethyl acetate and heated to boiling. The solution was filtered, and the ethyl acetate reduced in volume. A solid was obtained. This was recrystallized twice from ethyl acetate, m.p. 170-171°, lit.[43] m.p. 172-172.5°, (6 g., 0.026 mole, 34% yield).

trans-4-(4-Chlorophenyl)-Thiane-1-Oxide. This sulfoxide was prepared by the inversion of the configuration of the cis isomer according to the procedure of Johnson and McCants, Jr.[44] cis-4-(4-Chlorophenyl)-thiane-1-oxide (4 g., 0.016 mole) in 30 ml. of dry methylene chloride was added to triethyloxonium fluoroborate[45] and stirred for 30 min. at room temperature. Addition of anhydrous ether at 0° effected precipitation of the white, crystalline solid. The solid was washed with several portions of dry ethyl ether and dried under a stream of dry nitrogen. A solution of 0.2N sodium hydroxide (75 ml.) was added to the solid and stirred. The trans sulfoxide precipitated out as shiny platelets. The

product was recrystallized from ethyl acetate-hexane, m.p. 119-120, lit.[44] m.p. 120-120.5, (3 g., 0.013 mole, 80% yield).

II. Kinetic Procedures

A. Materials

The sulfoxides studied were obtained by the synthetic procedures described previously.

Baker and Adamson reagent grade 70% perchloric acid was used to prepare the stock acid solutions.

Mallinkrodt analytical reagent grade sodium iodide dried at 125° for several hours was used to prepare the sodium iodide stock solutions.

B. Preparation of Stock Solutions.

Sulfoxide solutions were prepared by weighing out the sulfoxide in a 10 ml. volumetric flask. The flask was flushed with a stream of pure nitrogen and capped with a serum cap. It was filled to the mark using a syringe containing perchloric acid stock solution.

Perchloric acid solutions were prepared by adding a calculated amount of concentrated perchloric acid to a 200 ml. volumetric flask. The flask was flushed with pure nitrogen and capped with a serum cap. Using a syringe, the flask was filled to the mark with distilled water which had been refluxed and cooled under a stream of pure nitrogen to remove dissolved oxygen. The flask was cooled in an ice bath during the addition of the distilled water.

Sodium iodide solutions were prepared by adding a calculated amount of dry sodium iodide to a 100 ml. volumetric flask. The flask was flushed with pure nitrogen and capped with a serum cap. Using a syringe, the flask was filled to the mark with oxygen free distilled water.

C. Preparation of Reaction Vessels.

The reaction vessels were 125 ml. Erlenmeyer flasks. Each flask was washed with a soap solution, rinsed, washed with acetone, rinsed several times with water and allowed to dry. The dry flask was flushed with pure nitrogen for several minutes and capped with a serum cap.

D. Preparation of Kinetic Solutions.

Each of the reaction vessels was first filled with 10 ml. of the sodium iodide solution by means of a syringe. Then 14 ml. of the perchloric acid solution was added to each of the reaction vessels by means of a syringe. The solution was stirred by gently swirling the flasks. The flasks were placed in a constant temperature bath set for $35 \pm 0.02^{\circ}C$. All runs were carried out at this temperature. After reaching bath temperature, 1 ml. of the sulfoxide solution was added to each of the reaction vessels by means of a syringe, and the time recorded at each addition. Each reaction vessel has a total volume of 25 ml. of solution. At the end of the appropriate time, each vessel was cooled and crushed ice added to quench the reaction. The iodine liberated by the reaction was titrated with standard sodium

thiosulfate solution, and the acid concentration of the runs was determined by titration with standardized 0.1N sodium hydroxide.

E. Determination of Rate Constants.

The pseudo first-order rate constants were obtained by plotting the log of the concentration vs. time and determining the slope of the line. The rate constant was obtained from the equation.

$$k = -2.303 \times (\text{slope})$$

The rate constant for the reduction of phenyl t-butyl sulfoxide was estimated, because under the conditions of the reaction, the rate of reduction was much slower than the oxidation of iodide ion by traces of dissolved oxygen in the kinetic solution. Therefore, the amount of iodine formed as the result of the reduction of the sulfoxide could not be determined with any degree of certainty.

SUMMARY

The purpose of the work presented in this dissertation was to determine the mechanism of the reduction of sulfoxides in acidic iodide ion solution. The results obtained provide information bearing on the mechanism of the reduction, but they do not permit the determination of the exact mechanism of this reaction.

The kinetics of the reduction of some phenyl alkyl and meta- and para-substituted phenyl methyl sulfoxides were studied in aqueous perchloric acid and sodium iodide. The kinetics of the reduction of cis- and trans-4-(4-chlorophenyl)-thiane-1-oxide were studied in aqueous acetic acid containing perchloric acid and sodium iodide.

It was found that the reduction was first-order with respect to sulfoxide, first-order with respect to iodide ion, and was acid catalyzed.

The basic nature of sulfoxides, the observed dependence of the rate on acid concentration, and previous work on the mechanism of this reaction by others are used as support for a rapid proton-sulfoxide equilibrium as the first step in the reaction. A plot of log $k_{obs.}$ versus $-H_o$ which resulted in a line with a slope close to two and the previous work done on the reduction in dimethyl sulfoxide by Krueger[5] are used to support the possibility of second-order dependence upon hydrogen ion for the reactions studied in this dissertation.

A study of the effect of increasing the size of the alkyl group on phenyl alkyl sulfoxides showed that, as the group was changed from methyl, ethyl, isopropyl to t-butyl, the rate of the reaction decreased. The interpretation of the decrease in reaction rate is complicated by the fact that increasing the size of the alkyl group can influence the equilibrium step as well as the rate-determining step. Several explanations are possible to explain the results obtained. Based upon the information available, it has been assumed that the decrease in rate observed for the alkyl phenyl sulfoxides can be due to a combination of the steric effects on the equilibrium step and the rate-determining step and that the steric effect upon the rate-determining step is the primary cause for the rate decrease.

Resonance and inductive effects on the reaction rate were determined by studying a series of meta- and para-substituted phenyl methyl sulfoxides. It was found that a plot of log $k_{obs.}$ versus σ resulted in a good straight line with a $\rho = -0.891$. The effect of substituents upon the rate-determining step was obtained by using the apparent pK_a values of these sulfoxides to account for substituent effects upon the equilibrium step. A plot of the log of the calculated constants for the rate-determining step versus σ resulted in a straight line with $\rho = +2.82$.

If it is assumed that the pK_a values used are proportional to those for the sulfoxides in the solvent system used in this study, the positive sign of rho indicates that there is a decrease

in positive charge on the reaction center in the transition state. The sign of rho is reasonable for a mechanism with iodide ion attack on the positive sulfur in an Sn2 type displacement.

A mechanism has been proposed for the reduction of the sulfoxides in this study. It consists of a rapid proton-sulfoxide equilibrium as the first step. This is followed by the rate-determining attack of iodide ion upon the protonated sulfoxide species with the displacement of a hydroxyl group aided by a hydronium-ion from the solvent. The resulting halosulfonium ion then undergoes rapid decomposition to products. This mechanism is speculative, but consistent with the data obtained.

The study of the cis- and trans-4-(4-chlorophenyl)-thiane-1-oxide showed the trans isomer was reduced faster than the cis isomer. A reason for the results observed is attributed to the possible formation of an acyloxysulfonium salt intermediate which undergoes attack by iodide ion with the displacement of an acetate ion.

Phenyl Methyl Sulfoxide

3.00M $HClO_4$, 0.20M NaI

Run I

time (min.)	c x 10^{-5} Mole	log c
20	12.08	-3.9179
40	11.65	-3.9337
60	11.26	-3.9485
80	10.85	-3.9646
100	10.54	-3.9772
120	10.06	-3.9974
140	9.68	-4.0141

$k_{obs.} = 2.99 \times 10^{-5}$ sec.$^{-1}$

Run II

60	12.26	-3.9115
120	10.98	-3.9594
180	9.77	-4.0101
240	9.06	-4.0429
300	8.16	-4.0883
360	7.63	-4.1175

$k_{obs.} = 2.79 \times 10^{-5}$ sec.$^{-1}$

Run III

60	11.83	-3.9270
120	10.97	-3.9598
180	10.12	-3.9948
240	9.24	-4.0343
300	8.49	-4.0711
360	7.89	-4.1029
420	7.43	-4.1290

$k_{obs.} = 2.36 \times 10^{-5}$ sec.$^{-1}$

Phenyl Methyl Sulfoxide

3.50M $HClO_4$, 0.20M NaI

Run I

time (min.)	c x 10^{-5} Mole	log c
30	10.96	-3.9602
60	9.37	-4.0283
90	8.04	-4.0947
120	7.02	-4.1537
150	6.10	-4.2147
180	5.46	-4.2628
210	5.01	-4.3002

$k_{obs.} = 7.55 \times 10^{-5}$ sec.$^{-1}$

Run II

30	11.02	-3.9578
60	9.38	-4.0278
90	8.18	-4.0873
120	7.20	-4.1427
150	6.34	-4.1979
180	5.33	-4.2733
210	4.90	-4.3098

$k_{obs.} = 7.17 \times 10^{-5}$

Run III

30	11.52	-3.9385
60	9.73	-4.0119
90	8.49	-4.0711
120	7.42	-4.1296
150	6.46	-4.1898
180	5.69	-4.2449
210	5.06	-4.2958

$k_{obs.} = 7.55 \times 10^{-5}$ sec.$^{-1}$

Phenyl Methyl Sulfoxide

4.00M $HClO_4$, 0.20M NaI

Run I

time (min.)	c x 10^{-5} Mole	log c
15	10.06	-3.9997
30	8.12	-4.0904
45	6.70	-4.1739
60	5.60	-4.2518
75	4.48	-4.3487
90	3.72	-4.4295

$k_{obs.}$: 22.08 x 10^{-5} $sec.^{-1}$

Run II

15	9.95	-4.0022
30	8.01	-4.0964
45	6.48	-4.1884
60	5.23	-4.2815
75	4.33	-4.3635
90	3.53	-4.4522

$k_{obs.}$: 22.62 x 10^{-5} $sec.^{-1}$

Run III

15	10.18	-3.9922
30	8.24	-4.0841
45	6.70	-4.2007
60	5.48	-4.2612
75	4.58	-4.3391
90	3.87	-4.4123
105	3.17	-4.4989

$k_{obs.}$: 22.35 x 10^{-5} $sec.^{-1}$

Phenyl Methyl Sulfoxide

4.50M $HClO_4$, 0.20M NaI

Run I

time (min.)	c x 10^{-5} Mole	log c
10	8.42	-4.0747
15	6.97	-4.1568
20	5.72	-4.2426
25	4.92	-4.3080
30	3.92	-4.4067
35	3.44	-4.4634

$k_{obs.} = 60.50 \times 10^{-5}$ sec.$^{-1}$

Run II

10	8.22	-4.0851
15	6.87	-4.1630
20	5.75	-4.2403
25	4.86	-4.3134
30	4.04	-4.3936
35	3.44	-4.4634

$k_{obs.} = 59.03 \times 10^{-5}$ sec.$^{-1}$

Run III

10	9.28	-4.0324
15	7.71	-4.1129
20	6.52	-4.1847
25	5.44	-4.2644
30	4.63	-4.3344
35	3.90	-4.4089

$k_{obs.} = 57.50 \times 10^{-5}$ sec.$^{-1}$

Phenyl Methyl Sulfoxide

4.00M $HClO_4$, 0.025M NaI

Run I

time (min.)	a x 10^{-2}M	b x 10^{-3}M	log $\frac{b}{a}(\frac{a-x}{b-x})$	log b
0	2.50	5.18	------	-----
15	2.47	5.01	0.0073	-2.300
30	2.46	4.93	0.0124	-2.307
45	2.44	4.84	0.0166	-2.315
60	2.42	4.76	0.0204	-2.322
75	2.40	4.64	0.0274	-2.334
90	2.39	4.60	0.0294	-2.337
105	2.37	4.49	0.0366	-2.348

$k_{obs.}$: 5.77 x 10^{-4} l/mole sec.

$k_{obs.}$: 1.78 x 10^{-5} $sec.^{-1}$

Run II

0	2.50	5.00	------	-----
30	2.45	4.76	0.0128	-2.322
60	2.42	4.58	0.0245	-2.339
90	2.38	4.40	0.0342	-2.357
120	2.35	4.27	0.0414	-2.370
150	2.33	4.14	0.0515	-2.383
180	2.30	4.00	0.0607	-2.398
210	2.28	3.88	0.0700	-2.411

$k_{obs.}$: 5.80 x 10^{-4} l/mole sec.

$k_{obs.}$: 1.78 x 10^{-5} $sec.^{-1}$

Phenyl Methyl Sulfoxide

4.0M $HClO_4$, 0.050M NaI

Run I

time (min.)	a x 10^{-2}M	b x 10^{-3}M	log $\frac{b}{a}(\frac{a-x}{b-x})$	log b
0	5.00	5.07	------	-----
30	4.80	4.60	0.0318	-2.337
60	4.74	4.28	0.0573	-2.369
90	4.68	3.95	0.0871	-2.403
120	4.63	3.70	0.1106	-2.438
150	4.57	3.44	0.1367	-2.463
180	4.52	3.36	0.1415	-2.474
210	4.51	3.12	0.1729	-2.506

$k_{obs.}$: 7.67 x 10^{-4} l/mole sec.

$k_{obs.}$: 4.21 x 10^{-4} $sec.^{-1}$

Run II

0	5.00	5.97	------	-----
30	4.89	5.41	0.0318	-2.267
60	4.80	5.00	0.0581	-2.301
90	4.73	4.61	0.0871	-2.336
120	4.66	4.30	0.1109	-2.367
150	4.61	4.02	0.1351	-2.396
180	4.55	3.72	0.1629	-2.430
210	4.51	3.52	0.1830	-2.444

$k_{obs.}$: 7.57 x 10^{-4} l/mole sec.

$k_{obs.}$: 4.21 x 10^{-5} $sec.^{-1}$

Phenyl Methyl Sulfoxide

4.0M $HClO_4$, 0.10M NaI

Run I

time (min.)	a x 10^{-2}M	b x 10^{-3}M	log $\frac{b}{a}(\frac{a-x}{b-x})$	log b
0	10.00	5.15	------	-----
30	9.81	4.23	0.0774	-2.374
60	9.67	3.53	0.1492	-2.452
90	9.57	3.01	0.2184	-2.521
120	9.47	2.54	0.2835	-2.595
150	9.41	2.21	0.3408	-2.656
180	9.35	1.91	0.4012	-2.719
210	9.30	1.65	0.4629	-2.783

$k_{obs.}$: 9.18 x 10^{-4} l/mole sec.

$k_{obs.}$: 8.43 x 10^{-5} $sec.^{-1}$

Run II

0	10.00	5.16	------	-----
30	9.81	4.24	0.0766	-2.373
60	9.66	3.50	0.1529	-2.456
90	9.55	2.95	0.2220	-2.530
120	9.47	2.51	0.2889	-2.600
150	9.39	2.13	0.3564	-2.672
180	9.33	1.86	0.4126	-2.731
210	9.29	1.66	0.4594	-2.780

$k_{obs.}$: 9.18 x 10^{-4} l/mole sec.

$k_{obs.}$: 8.93 x 10^{-5} $sec.^{-1}$

Phenyl Methyl Sulfoxide

$4.0M\ HClO_4$, 0.20M NaI

Run I

time (min.)	a x 10^{-2}M	b x 10^{-3}M	log $\frac{b}{a}(\frac{a-x}{b-x})$	log b
0	20.00	5.03	------	-----
15	19.80	4.02	0.0920	-2.396
30	19.64	3.25	0.1807	-2.488
45	19.53	2.68	0.2622	-2.572
60	19.44	2.24	0.3401	-2.650
75	19.35	1.79	0.4335	-2.747
90	19.30	1.49	0.5120	-2.827

$k_{obs.}$: 10.83×10^{-4} l/mole sec.

$k_{obs.}$: 22.08×10^{-5} $sec.^{-1}$

Run II

0	20.00	5.20	------	-----
15	19.79	4.07	0.1078	-2.390
30	19.63	3.30	0.1892	-2.482
45	19.51	2.68	0.2772	-2.572
60	19.41	2.19	0.3625	-2.660
75	19.34	1.83	0.4390	-2.738
90	19.28	1.55	0.5097	-2.810
105	19.23	1.27	0.5952	-2.896

$k_{obs.}$: 10.63×10^{-4} l/mole sec.

$k_{obs.}$: 22.35×10^{-5} $sec.^{-1}$

Phenyl Methyl Sulfoxide

4.0M $HClO_4$, 0.30M NaI

Run I

time (min.)	a x 10^{-2}M	b x 10^{-3}M	log $\frac{b}{a}\left(\frac{a-x}{b-x}\right)$	log b
0	30.00	5.28	------	-----
10	29.78	4.04	0.1129	-2.394
20	29.59	3.09	0.2266	-2.510
30	29.46	2.47	0.3220	-2.607
40	29.36	1.94	0.4255	-2.712
50	29.28	1.55	0.5218	-2.810
60	29.22	1.26	0.6108	-2.900
70	29.17	1.02	0.7018	-2.991

$k_{obs.}$: 12.62 x 10^{-4} 1/mole sec.

$k_{obs.}$: 37.50 x 10^{-5} $sec.^{-1}$

Run II

0	30.00	4.98	------	-----
10	29.75	3.69	0.1265	-2.433
20	29.59	2.91	0.2274	-2.536
30	29.47	2.30	0.3278	-2.638
40	29.40	1.94	0.4007	-2.712
50	29.31	1.51	0.5081	-2.821
60	29.25	1.19	0.6107	-2.924
70	29.21	0.99	0.6900	-3.004

$k_{obs.}$: 12.35 x 10^{-4} 1/mole sec.

$k_{obs.}$: 36.67 x 10^{-5} $sec.^{-1}$

Phenyl Methyl Sulfoxide

$4.0M\ HClO_4$, 0.2M NaI, $2.5 \times 10^{-5}M\ I_2$

Run I

time (min.)	c x 10^{-5} Mole	log c
15	9.95	-4.0022
30	8.01	-4.0964
45	6.48	-4.1884
60	5.23	-4.2815
75	4.33	-4.3635
90	3.53	-4.4522

$k_{obs.} = 22.62 \times 10^{-5}\ sec.^{-1}$

Run II

$4.0M\ HClO_4$, 0.20M NaI, $4.0 \times 10^{-5}M$ Sulfide

15	9.97	-4.0013
30	8.14	-4.0894
45	6.73	-4.1720
60	5.48	-4.2612
75	4.42	-4.3546
90	3.61	-4.4425

$k_{obs.} = 22.83 \times 10^{-5}\ sec.^{-1}$

Phenyl Methyl Sulfoxide

4.0M $HClO_4$, 0.20M NaI, 0.001M Sulfoxide

Run #1

time (min.)	c x 10^{-5} Mole	log c
10	2.41	-4.6180
20	2.24	-4.6497
30	2.04	-4.6904
40	1.69	-4.7721
50	1.48	-4.8297
60	1.35	-4.8697
70	1.30	-4.8861

$k_{obs.} = 22.45 \times 10^{-5}$ sec.$^{-1}$

Run #1

4.0M $HClO_4$, 0.20M NaI, 0.10M Sulfoxide

11	22.04	-3.6568
17	20.68	-3.6844
20	19.60	-3.7077
25	18.39	-3.7354
30	17.47	-3.7577
35	16.11	-3.7929

$k_{obs.} = 22.23 \times 10^{-5}$ sec.$^{-1}$

Phenyl Ethyl Sulfoxide

4.0M $HClO_4$, 0.20M NaI

Run I

time (min.)	c x 10^{-5} Mole	log c
20	10.54	-3.9772
40	8.72	-4.0595
60	7.41	-4.1302
80	6.36	-4.1965
100	5.36	-4.2708
120	4.54	-4.3429

$k_{obs.} = 13.92 \times 10^{-5}$ sec.$^{-1}$

Run II

20	10.30	-3.9872
40	8.79	-4.0472
60	7.16	-4.1451
80	6.25	-4.2041
100	5.33	-4.2733
120	4.59	-4.3382

$k_{obs.} = 13.50 \times 10^{-5}$ sec.$^{-1}$

Phenyl Isopropyl Sulfoxide

4.0M $HClO_4$, 0.20M NaI

Run I

time (min.)	c x 10^{-5} Mole	log c
30	13.01	-3.8857
60	12.96	-3.8874
90	12.86	-3.8908
120	12.75	-3.8945
150	12.65	-3.8979
180	12.55	-3.9014
210	12.44	-3.9052

$k_{obs.}$: 0.449 x 10^{-5} $sec.^{-1}$

Run II

60	12.65	-3.8979
120	12.49	-3.9034
180	12.23	-3.9126
240	12.10	-3.9172
300	11.95	-3.9226
360	11.63	-3.9344

$k_{obs.}$: 0.460 x 10^{-5} $sec.^{-1}$

Run III

30	12.70	-3.8962
60	12.66	-3.8976
90	12.56	-3.9000
120	12.48	-3.9038
150	12.38	-3.9073
180	12.22	-3.9129
210	12.03	-3.9197

$k_{obs.}$: 0.460 x 10^{-5} $sec.^{-1}$

p-Tolyl-Methyl Sulfoxide

4.00M $HClO_4$, 0.20M. NaI

Run II

time (min.)	c x 10^{-5} Mole	log c
10	10.22	-3.9905
20	8.48	-4.0716
30	6.97	-4.1568
40	5.70	-4.2441
50	4.75	-4.3233
60	3.98	-4.4001
70	3.71	-4.4306

$k_{obs.} = 32.20 \times 10^{-5}$

Run III

10	10.29	-3.9876
20	8.50	-4.0706
30	6.90	-4.1561
40	5.78	-4.2381
50	4.81	-4.3178
60	3.76	-4.4248
70	3.18	-4.4976

$k_{obs.} = 31.82 \times 10^{-5}$

Run IV

10	10.51	-3.9784
20	8.68	-4.0615
30	7.19	-4.1433
40	5.91	-4.2284
50	5.07	-4.2950
60	4.14	-4.3830
70	3.42	-4.4660

$k_{obs.} = 31.05 \times 10^{-5}$

m-Tolyl Methyl Sulfoxide

4.0M $HClO_4$, 0.20M NaI

Run I

time (min.)	c x 10^{-5} Moles	log c
10	11.15	-3.9527
20	9.51	-4.0218
30	8.11	-4.0910
40	7.00	-4.1549
50	5.97	-4.2240
60	5.29	-4.2765
70	4.42	-4.3546

$k_{obs.} = 25.68 \times 10^{-5}$ sec.$^{-1}$

Run II

10	10.58	-3.9755
20	9.24	-4.0343
30	7.79	-4.1085
40	6.56	-4.1831
50	5.69	-4.2449
60	4.85	-4.3143
70	4.32	-4.3645

$k_{obs.} = 25.83 \times 10^{-5}$ sec.$^{-1}$

Run III

10	10.04	-3.9983
20	8.67	-4.0620
30	7.33	-4.1349
40	6.20	-4.2076
50	5.50	-4.2596
60	4.65	-4.3325
70	3.98	-4.4001

$k_{obs.} = 25.30 \times 10^{-5}$ sec.$^{-1}$

p-Chlorophenyl Methyl Sulfoxide

Run I

time (min.)	c x 10^{-5} Moles	log c
5	12.71	-3.8958
10	12.08	-3.9179
20	11.17	-3.9579
30	10.67	-3.9718
40	9.73	-4.0119

$k_{obs.} = 12.65 \times 10^{-5}$ sec.

Run II

10	11.41	-3.9427
20	10.70	-3.9706
30	9.96	-4.0017
40	9.10	-4.0410
50	8.44	-4.0737
60	7.74	-4.1113
70	7.24	-4.1403

$k_{obs.} = 13.03 \times 10^{-5}$ sec.$^{-1}$

Run III

10	11.55	-3.9374
20	10.69	-3.9710
30	9.84	-4.0070
40	9.15	-4.0386
50	8.46	-4.0726
60	7.73	-4.1118
70	7.09	-4.1493

m-Chlorophenyl Methyl Sulfoxide

Run III

time (min.)	c x 10^{-5} Mole	log c
15	11.40	-3.9431
41	11.00	-3.9586
45	9.79	-4.0092
62	8.94	-4.0487
75	8.32	-4.0799
90	7.74	-4.1113
105	7.03	-4.1547

$k_{obs.} = 8.70 \times 10^{-5}$ sec.$^{-1}$

Run IV

15	11.66	-3.9333
30	10.79	-3.9670
45	10.06	-3.9974
60	9.48	-4.0232
75	8.40	-4.0757
90	7.84	-4.1057
105	7.37	-4.1325

$k_{obs.} = 8.43 \times 10^{-5}$ sec.$^{-1}$

Run V

15	11.43	-3.9419
30	10.42	-3.9821
45	9.52	-4.0214
60	8.89	-4.0511
75	8.15	-4.0888
90	7.43	-4.1290
105	6.48	-4.1884

$k_{obs.} = 9.05 \times 10^{-5}$ sec.$^{-1}$

p-Nitrophenyl Methyl Sulfoxide

Run I

time (min.)	c x 10^{-5} Mole	log c
30	11.39	-3.9435
60	10.20	-3.9914
90	9.30	-4.0315
120	8.52	-4.0696
150	7.82	-4.1068
180	7.16	-4.1451

$k_{obs.} = 4.87 \times 10^{-5}$ sec.$^{-1}$

Run II

30	11.39	-3.9435
60	10.23	-3.9901
90	9.65	-4.0155
120	8.87	-4.0521
150	8.04	-4.0947
180	7.19	-4.1433
210	6.73	-4.1720

$k_{obs.} = 4.98 \times 10^{-5}$ sec.$^{-1}$

Run III

30	11.13	-3.9535
60	10.31	-3.9869
90	9.27	-4.0329
120	8.51	-4.0701
150	7.82	-4.1068
180	7.09	-4.1493
210	6.12	-4.2132

$k_{obs.} = 5.09 \times 10^{-5}$ sec.$^{-1}$

m-Nitrophenyl Methyl Sulfoxide

Run I

time (min.)	c x 10^{-5} Mole	log c
30	11.45	-3.9412
60	10.98	-3.9594
90	10.35	-3.9851
120	9.72	-4.0123
150	9.22	-4.0353
180	8.58	-4.0665
210	8.16	-4.0883

$k_{obs.} = 3.33 \times 10^{-5}$ sec.$^{-1}$

Run II

30	11.84	-3.9266
60	11.08	-3.9555
90	10.49	-3.9792
120	10.66	-3.9722
150	9.54	-4.0204
180	8.79	-4.0560
210	8.76	-4.0575

$k_{obs.} = 3.33 \times 10^{-5}$ sec.$^{-1}$

Run III

30	11.54	-3.9378
60	10.97	-3.9579
90	10.16	-3.9931
120	9.56	-4.0295
150	9.07	-4.0424
180	8.45	-4.0731
210	7.95	-4.0996

$k_{obs.} = 3.45 \times 10^{-5}$ sec.$^{-1}$

p-Methoxyphenyl Methyl Sulfoxide

Run I

time (min.)	c x 10^{-5} Mole	log c
5	11.24	-3.9492
10	10.50	-3.9788
15	9.58	-4.0186
20	8.83	-4.0540
25	8.09	-4.0920
30	7.49	-4.1255
35	6.95	-4.1580

$k_{obs.} = 27.60 \times 10^{-5}$ sec.$^{-1}$

Run III

5	11.34	-3.9454
10	10.31	-3.9867
15	9.52	-4.0214
20	8.71	-4.0600
25	8.13	-4.0899
30	7.38	-4.1319
35	6.81	-4.1668

$k_{obs.} = 27.60 \times 10^{-5}$ sec.$^{-1}$

Run IV

5	12.62	-3.8989
10	12.02	-3.9201
15	10.81	-3.9662
20	10.05	-3.9978
25	9.30	-4.0415
30	8.54	-4.0685

$k_{obs.} = 26.99 \times 10^{-5}$ sec.$^{-1}$

m-Methoxyphenyl Methyl Sulfoxide

Run V

time (min.)	c x 10^{-5} Mole	log c
10	12.12	-3.9165
20	11.00	-3.9586
30	9.98	-4.0009
40	9.15	-4.0386
50	8.38	-4.0768
60	7.74	-4.1113
70	7.09	-4.1493

$k_{obs.} = 14.95 \times 10^{-5}$ sec.$^{-1}$

Run VI

10	11.77	-3.9292
20	10.71	-3.9702
30	9.78	-4.0097
40	8.96	-4.0477
50	8.05	-4.0942
60	7.49	-4.1255
70	6.89	-4.1618

$k_{obs.} = 14.84 \times 10^{-5}$ sec.$^{-1}$

Run VII

10	12.22	-3.9129
20	11.28	-3.9477
30	10.24	-3.9897
40	9.43	-4.0255
50	8.55	-4.0680
60	8.04	-4.0947
70	7.36	-4.1331

$k_{obs.} = 14.95 \times 10^{-5}$ sec.$^{-1}$

cis-4-(4-Chlorophenyl)-Thiane-1-Oxide

4.0M $HClO_4$, 0.20M NaI, H_2O/HOAc (solvent)

Run I

time(min.)	c x 10^{-5} Mole	log c
60	9.22	-4.0353
90	8.59	-4.0660
120	8.04	-4.0947
150	7.50	-4.1249
180	6.84	-4.1649
210	6.24	-4.2048

$k_{obs.} = 4.26 \times 10^{-5}$ sec.$^{-1}$

Run II

15	10.64	-3.9731
30	10.20	-3.9914
45	9.76	-4.0105
60	9.39	-4.0273
75	9.05	-4.0433
90	8.57	-4.0670
105	8.30	-4.0809

$k_{obs.} = 4.60 \times 10^{-5}$ sec.$^{-1}$

trans-4-(4-Chlorophenyl)-Thiane-1-Oxide

Run I

15	1.70	-4.7695
20	1.48	-4.8297
25	1.06	-4.9747
30	0.72	-5.1427

Phenyl t-Butyl Sulfoxide

4.0M $HClO_4$, 0.20M NaI

time (hr.)	$I_2 \times 10^{-5}$, M	Sulfoxide $\times 10^{-5}$, M*	log (S 0)
0	----	12.56	-3.9010
3	0.79	11.77	-3.9292
6	0.82	11.74	-3.9303
9	0.85	11.71	-3.9318
12	0.89	11.67	-3.9329
15	0.94	11.62	-3.9348
18	0.98	11.58	-3.9363

$$k_{obs.} = 0.035 \times 10^{-5} \text{ sec.}^{-1}$$

* Calculated concentration of sulfoxide remaining based on the amount of iodine formed without correcting for iodine formed due to oxygen in the reaction sample. A blank indicated that 0.88×10^{-5} mole of iodine was formed due to the presence of oxygen after 18 hr. of reaction time. Correcting for the amount of iodine formed due to oxygen, the concentration of sulfoxide remaining after 18 hr. was 12.46×10^{-5} mole. Plotting the log of this concentration and the initial concentration versus time resulted in the following estimated rate constant:

$$k_{obs.} = 0.012 \times 10^{-5} \text{ sec.}^{-1}$$

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